ALTERNATIVE FUELS

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BOOKS ARCADE

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CHAPTER 1

BASICS OF ALTERNATIVE FUEL

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In all regions of the globe, internal combustion engines that use conventional and unconventional fuels are a necessary element of daily life. In all types of motor vehicles, power generating, and other applications, they are almost widely utilised. Liquid fuels have been the standard for internal combustion engines. From petroleum, these fuels are distilled. Consider using heavy fuel oil, kerosene, diesel, or gasoline.However, engines may run on a variety of fuels besides liquid fossil fuels, which are practical and inexpensive. As long as internal combustion engines have existed, other fuels have really been accessible. For instance, during World War II, many vehicles ran on wood gas, a fuel. Saving gasoline for the war effort was made possible as a result. By burning wood chips just partially, wood gas was produced. In a fashion similar to a big kettle, the procedure would happen. The kettle might be towed behind a car on a trailer, where it would then be connected via a pipe to the engine.

Though wood gas is no longer widely used in transportation, there are a number of different alternative fuels that are, and are still being developed, accessible. Some of them, like liquefied petroleum gas (LPG—a mixture of propane and butane) and compressed natural gas (CNG), are made from fossil fuels. Others, including biodiesel, ethanol, biogas, and renewable diesel, are made from organic waste or energy crops. If you'd want to understand more, you may look up what low-carbon fuels are.

Using renewable power and non-fossil feedstock like carbon dioxide (CO_2) and water, advances in chemical engineering and other fields have also made it feasible to synthesis methane, hydrogen, fuel, and more. Sometimes referred to as e-fuels, these synthetic fuels are. To understand more, you may look up information on power-to-x and e-fuels. As a direct substitute, renewable diesel is available. None are necessary for the majority of engines. In order to be utilised in conventional compression ignition (CI) engines, biodiesel must be mixed with fossil fuel. When combined with gasoline, ethanol, which is essentially alcohol, may be utilised in conventional SI (spark ignition) cars. It is quite frequent to combine ethanol. Diesel and gasoline, both liquid hydrocarbon fuels, have historically dominated the world's transportation industry. Years of work have gone into creating alternative fuels, even if the reasons for doing so have changed. Reductions in exhaust emissions throughout the 1990s helped to justify the development of alternative fuels in North America and Europe. In order to mitigate climate change emissions, lessen reliance on petroleum imports, improve energy security, and ultimately address the depletion of crude oil resourceswhich are finite and non-renewable current developments are justified by a decreased reliance of the transportation sector on fossil fuels, particularly on oil.

While a suitable, technically possible, and economically viable diesel and gasoline substitute has not yet been produced, a few alternative fuels have made headway in the fuel markets. Natural gas, biodiesel, or ethanol (made from maize in North America or sugar cane in Brazil) are a few of them. Other alternative fuels might be categorised as experimental or niche fuels. Future improvements are possible, such as those in the field of synthetic electrofuels.

An alternative fuel must satisfy a number of requirements in order to be a practical substitute for petroleum-based fuels. These requirements include: Energy density and the foundation of resourcesThe alternative fuel must have a large resource base (feedstock) and a high energy density (measured in W/m2) in order to replace a significant portion of conventional fuel. The low energy density and large land need of biofuels, as well as wind and solar energy, are frequent characteristics.

Energy return on investment (EROI) The alternative fuel should be generated using the least amount of input (fossil) energy as feasible. EROI begins to decline into the low single digits or even approaches one (as is the case with some biofuels), which makes the production process self-defeating and more resembles the wasteful conversion of petroleum into an alternative energy source than the extraction of additional energy from the environment. One of the telltale indicators of poor EROI fuels is their high cost, which reflects the large energy input during production. Since these fuels cannot compete with petroleum, they must be supported in the market by government mandates or subsidies. Characteristics of a renewable resource and low carbon emissions The fuel should be produced from a natural resource that can either be replenished by new growth or is perpetually available in order to minimise climate consequences. The energy sources biomass and wind/solar are suitable examples. Biomass and other resources that rely on regrowth are renewable, but their capacity to be replenished depends on how quickly they are harvested. This means that they may be used up beyond the point at which they can no longer be replenished. Wood, for example, is not always a renewable resource, especially in light of the planet's continuing deforestation.

Biomass, natural gas, and, in the long run, electrofuels (also known as e-fuels or eFuels) generated from renewable energy are the primary alternative fuel sources that have been deemed promising. It should be emphasised that natural gas is not renewable, and synthetic electrofuels often have poor EROI and low life cycle energy efficiency, therefore these fuel alternatives do not fully satisfy the aforementioned requirements. Common Specifications. Prior to an alternative fuel's widespread adoption for use in current powertrains, its compatibility with engines—whether the normal diesel/gasoline engine or a modified engine design—must be ensured, including any short- and long-term consequences. Specifically, it is necessary to create and establish standard standards for all pertinent fuel attributes. The following are a few things that the standard standards must protect or cover

1. the need for any additives in gasoline (e.g., lubrication)
2. the effects of fuel impurities on additives
3. Standardized test procedures are accessible.

World Energy Consumption

World energy consumption has been steadily increasing for a variety of reasons, including improved quality of life, population growth, industrialization, rapid economic growth in developing countries, and increased people transportation.and goods, etc. There are numerous types of fuel available worldwide, with demand strongly influenced by application and to use, location and regional resources, cost, "cleanness" and environmental impact factors, generation and utilisation safety, socioeconomic factors, global and regional politics, and so on.

The energy utilisation cycle is divided into three stages: generation, distribution, and consumption, everything the of which must be carefully balanced in order to achieve an ideal energy infrastructure. As a limiting factor, any bottlenecking or shortage would have an immediate impact on the entire cycle. If the production of one type of fuel declines, so will the distribution and consumption of that fuel, making fuel switching from one type to another, as well as forced conservation, inevitable. Furthermore, the consumer price of this fuel type might undoubtedly rise due to the supply and demand principle. Even a breakdown in the transportation system of a specific fuel type would have a direct impact on the consumer market, with consequences such as fuel shortages and price increases occurring for at least a limited time in the affected region.

Petroleum

For this period, world petroleum consumption has grown at an average rate of 1.04% a year. Although this rate of increase appears to be moderate, it should be noted that petroleum resources are limited and can deplete over time.

Professionals and policymakers have frequently estimated the number of years for which petroleum can be supplied and devoured at current consumption rates, but the figures have been inconsistent and fluctuating from year to year. The difficulty in estimating the future recoverable amount of petroleum from all proved and unproven reserv6es contributes to this uncertainty. The Society of Petroleum Engineers (SPE) and the World's Oil Council (WPC) have developed and approved several definitions of petroleum reserve-related terms to help professionals use these terms consistently.

Proved reserves are the quantities of petroleum that can be estimated with reasonable certainty to be commercially recoverable from known reservoirs and under current economic conditions, methods of operation, and government regulations based on an analysis of geological and engineering data. Proven reserves are further classified as either developed or undeveloped.

Unproved reserves are based on geologic and engineering data similar to that used in estimates of proved reserves, but technical, contractual, economic, or regulatory uncertainties preclude such reserves being classified as proved. Unproven reserves are further subdivided into probable and possible reserves. Probable reserves are unproven reserves that, based on geological and engineering data, appear to be more likely than not to be recoverable. If a probabilistic perception is to be provided.

According to the Oil and Gas Journal (OGJ), global petroleum reserves were 1.27 trillion barrels at the start of 2004. 5 This estimate is 53 billion barrels higher than the previous year (2003), owing to new discoveries, improved technology, and shifting economics. 5 einsteineruploading up to get together with Because of rising gas prices and growing environmental concerns, many Americans are looking for better alternatives to traditional gasoline-powered automobiles. Consumers have been wary of alternatives including such diesel, gas-electric hybrids, all-electric vehicles, hydrogen, and ethanol due to misinformation, confusion, and biassed public opinion. With gasoline prices reaching all-time highs across the country, there has been a surge in interest in these vehicles. It is obvious that clear and unbiased information on this subject is difficult to find. The inquiries will be of interest to anyone who owns or plans to own a passenger or sport utility vehicle due to in-depth research that includes overall life-cycle cost, comparisons, and an analysis of other studies on the subject.

Life costs, cost-to-benefit ratios, vehicle comparisons, and performance statistics will be included in the findings. The analysis will be divided into three groups; 20% city - 80% highway, and 80% city -20% highway. These figures will be based on the following assumptions: 100,000 mile life span over ten years, every vehicle will be purchased new at the MSRP (Manufacturer's Suggested Retail Price) including shipping and receiving, they will be driven in a similar manner, recommended factory service maintenance intervals will be followed, and fuel prices will be calculated from the peak prices as of July 17th, 2008. The goal of this research is to educate the general public about the financial and environmental concerns about gasoline alternatives.

Natural Gas

Natural gas has grown in popularity in a variety of industrial sectors in recent years. It burns cleaner than coal or petroleum, benefiting the environment. It is primarily distributed through pipelines and is transported across oceans by tankers in a liquid state (known as liquefied natural gas [LNG]). shows the global consumption of dry fossil fuels by region and country from 1980 to 2003.

Global natural gas consumption has steadily increased at a rate of 2.6% per year. The world natural gas reserve as of January 1, 2004 was 6079 trillion cubic feet, according to the Oil and Gas Journal (OGJ)5. Assuming that global natural gas consumption remains constant, the reserve would be sufficient to last for another 64 years, assuming that factors such as increased yearly consumption, the discovery of new deposits, and technological advances such as the use of natural gas hydrates are not taken into account. Despite the fact that this rough estimate appears to be slightly better than that of petroleum, the fate of natural gas is similar to that of petroleum.

shows the worldwide distribution of natural gas for countries with major reserves. Projection of global natural gas reserves has generally increased, at least in terms of numbers, due to new discoveries of major natural gas fields, the estimated reserves of which exceed annual consumption. einsteineruploading up to get together with (at 2518 trillion cubic feet). 5,8 In terms of natural gas consumption, the U.S. accounts for 23.4% (based on statistics for 2003), whereas Asia and Oceania account for 13%. This is in stark contrast to the consumption pattern for petroleum, the world's most popular transportation fuel. Natural gas energy can be obtained from other sources or replaced by other types of energy, depending on the infrastructure and supply-and-demand system of a region.

Natural gas is the third most-used energy source in the U.S. (23%) after petroleum and coal. Manufacturers, public utilities, residential consumers (heating homes and cooking), and commercial users, primarily for heating buildings, are the largest users of natural gas. Natural gas helps manufacture a wide variety of goods including plastics, fertilisers, photographic films, inks, synthetic rubber, fibres, detergents, glues, methanol, ethers, insect repellents, and much more. 9 It is also used in the generation of electricity because it burns cleaner and more efficiently than coal and has fewer emission-related issues than other popular fossil fuels. Despite the fact that it can be used in standard internal combustion engines, natural gas has a small market share as a transportation fuel. einsteineruploaded with. Natural gas is the primary heating fuel in more than half of all homes in the United States.

Because natural gas is heavily used by both electric power generating utilities and homes, any major disruption in natural gas supply would have unique but grave consequences in the nation's energy management, at least in the short term and for a specific affected region. The regional energy drug dependency problem has been somewhat alleviated by utility deregulation, which has changed the business practises of electric utilities and the natural gas industry. Customers can benefit from deregulation.

Coal

einsteinerupload of. Coal consumption accounted for 24% of total global energy consumption in 2002. Approximately 65% of coal consumption was used for electric power generation, 31% for industrial consumers such as steel manufacturers and steam generators, and a significant portion of the remaining 4% for residential and commercial consumers. Coal was once a popular transportation fuel for powering steam engines; however, coal is now rarely used in transportation. This graph depicts global coal consumption by region and country from 1980 to 2003. According to the Energy Information Administration's (EIA)10 forecast for 2025, global consumption of coal for electric power generation and industrial use would remain relatively stable.

The slight increase in industrial consumption is primarily due to China's rapid industrial growth, which has an abundant reserve and supply of coal but a limited reserve of oil and natural gas. International coal trade is expected to grow from 714 million tonnes in 2003 to 969 million tonnes in 2025, accounting for 12 to 13% of total global coal consumption during this time period. Total recoverable reserves of coal around the world are estimated at 1001 billion tons,11 which would be enough to last approximately 184 years if maintained at the 2003 consumption level of 5.439 billion tonnes. The reserve amount was recently reduced after stricter criteria, namely safe and economical recoverability, were applied. Despite the fact that coal deposits are found all over the world, approximately 57% of the world's recoverable coal reserves are concentrated in three countries: U.S. (27%), Russia (17%), and China (13%). Following these three, India, Australia, South Africa, Ukraine, Kazakhstan, and Yugoslavia account for 33% of total reserves. Coal, like other fossil fuels such as petroleum and natural gas, is highly unequally and unevenly distributed. In 2002, the United States consumed 1066 million tonnes of coal.

Consumption is expected to steadily increase to 1505 million tonnes by 2025. The United States' reliance on coal for electric power generation is expected to continue. The United States' reliance on coal consumption for electricity generation fell from 56% in the mid-1990s to 52% in 2002. It is projected to decline slightly from 52% in 2002 to 51% in 2015 and then return to 53% in 2025. This prediction takes into account the expected growth in additional coal-fired power plants, as well as the expected increase in the average utilisation rate of coal-fired power generation capacity, from 70% in 2002 to 83% in 2025. a matter of a few minutes. Coal has been a focal target for synthetic conversion into other forms of fuel, i.e., synfuels, owing to its relative abundance and stable fuel price on the market. R&D work has seen ups and downs due to external factors such as the comparative carbon fuels market and the era's international energy outlook. Coal can be gasified, liquefied, pyrolyzed, and coprocessed with oil, biomass, scrap tyres, and municipal solid waste. Secondary conversion of coal-derived gas and liquids can generate a wide array of petrochemical products, as well as alternative fuels. Coal was the second largest source of carbon dioxide emissions from the consumption and flaring of fossil fuels in 2003, accounting for 37% of total emissions. Petroleum consumption was the leading primary reason for emissions of carbon dioxide, accounting for 42% of total emissions. Natural gas came in third place with 21%.

Renewable Energy

Because all fossil fuels are nonrenewable, they will eventually be depleted. They will become expensive because they are based on finite resources and their distribution is heavily localised in certain parts of the world. Furthermore, the production of energy from fossil fuels necessitates combustion, which pollutes the environment and emits greenhouse gases. Renewables is the obvious choice for ensuring the world's future with a clean environment and nondepleting energy resources. Renewable energy sources include: solar energy, wind energy, geothermal energy, biomass, and hydrogen. Except for geothermal energy, the majority of renewable energy is derived directly or indirectly from the sun's rays. Renewable energy has numerous advantages, which include:

1. Environmental purity with no pollutant emissions
2. The absence of depletion
3. International accessibility
4. There is no cause for global warming.
5. Waste reduction
6. Energy cost stabilisation
7. Employment creation

From 2000 to 2004, energy consumption was broken down by energy source. As can be seen in this comparative list, renewable energy accounts for only about 6% of total energy consumption. With increases in petroleum and natural gas prices, such as those seen in 2005 and 2006, the relative competitive edge of renewable and alternative fuels improves dramatically. Furthermore, technological advances in alternative renewable energy fields, as well as public awareness backed by strong governmental support and incentives, make the future of alternative and renewable energy very promising. From 1993 to 2003, global geothermal, solar, wind, wood, and waste electric power generation increased at a 6.8% annual rate.

The United States led the world with 94 billion kilowatt-hours, followed by Germany (31 billion), Japan (28 billion), Spain (16.3 billion), and Brazil (16.2 billion). In 2003, these five countries accounted for roughly 60% of global geothermal, solar, wind, wood, and waste power production. Corn ethanol is increasingly being used as a gasoline blend fuel. One new brand is E85, which contains 85% ethanol and 15% gasoline. Many gas stations in the United States have begun to stock E85 fuels on a regular basis, and many automakers are offering multiple lines of vehicles that can run on either conventional gasoline or E85. The phase-out of MTBE (methyl tertiary-butyl ether), once the most popular oxygenated blend fuel, has accelerated the use of ethanol as an oxygenated gasoline blend fuel in many U.S. states.

The general public's interest in clean-burning, energy-efficient hydrogen has sparked unprecedented interest in hydrogen technology and fuel cell research and development. Many experts predict the future to be a hydrogen economy. For the hydrogen economy to be realised, a long list of technological advances must be accomplished, which include technologies for inexpensive generation, safe distribution and storage, safe and efficient materials for hydrogen handling, hydrogen internal combustion engine, hydrogen fuel cells, loss prevention, etc. Energy generation from biomass and city and county solid waste (MSW) is also promising in areas with limited landfill space. Field technological advances have made this option efficient and environmentally safe.

Gasification of Coal

Conversion of coal via any of the processes to produce a mixture of combustible gases is termed coal gasification, even though a large number of chemical reactions other than so-called gasification reactions are involved. Even though the product gases of coal gasification involve combustible chemical species, the purpose of gasification is not limited to generation of gaseous fuel, because the product gas can be easily processed to generate other valuable chemical and petrochemical feedstock. Commercial coal gasification entails the controlled partial oxidation of coal to produce desired gaseous products.

The coal can be heated directly through combustion or indirectly through another heat source. To provide intimate molecular contact for chemical reaction, a gasifying medium is typically passed over (or through) the heated coal. To produce gaseous products, the gaseous reactants react with carbonaceous coal matters (i.e., coal hydrocarbons) or with other primary coal decomposition products. Not all of the gaseous products produced by such processes are desirable in terms of fuel quality, further processing, and environmental concerns. As a result, coal gasification is always carried out in tandem with downstream processes, not only for final applications but also for gas cleaning. The primary focus of coal gasification may be on electricity generation via integrated gasification combined cycle (IGCC) types, syngas production for pipeline applications, hydrogen production, or synthesis of liquid fuels and petrochemicals as alternative raw materials sources. With the emergence of a hydrogen economy, coal gasification's role in hydrogen generation may become even more important.

Coal conversion from solid to gaseous fuel (or gaseous chemical) is a common practise today. Earlier (1920-1940), coal gasification was used to produce manufactured gas in hundreds of plants around the world, and such plants were known as manufactured gas plants (MGPs). Because of the abundant supply of petroleum and natural gas at reasonable prices after WWII, this technology became obsolete. With the onset of the oil embargo in the early 1970s and subsequent increases and fluctuations in petroleum prices, as well as the natural gas and petroleum shortages experienced at the start of the twenty-first century, interest in coal gasification and its further commercial exploitation was reignited. Recently, as interest in fuel cell technology has grown, so has interest in coal gasification as a means of obtaining dependable and low-cost hydrogen sources. Many major activities in coal gasification research, development, and demonstration have recently led to significant improvements in conventional technology, making coal gasification more competitive in modern fuel markets.

Tampa Electric Company's Polk Power Station near Mulberry, FL, is the nation's first "greenfield" (built as a brand new plant, not a retrofit) commercial gasification combined cycle power station. The plant, which opened in 1997, is able to produce 313 MW of electricity while also removing more than 98% of sulphur from coal that is converted into commercial products. The Wabash River Coal Gasification Repowering Project, located outside West Terre Haute, IN, was the first full-scale commercial gasification combined cycle plant built in the United States. In November 1995, the plant began full operation. The plant, which can generate 292 MW of electricity, is still one of the world's largest single-train IGCCs in commercial operation.

Coal gasification includes a series of reaction steps that convert coal containing C, H, and O, as well as impurities such as S and N, into synthesis gas and other forms of hydrocarbons. In general, this conversion is accomplished by introducing a gasifying agent (air, oxygen, and/or steam) into a reactor vessel containing coal feedstock and controlling the temperature, pressure, and flow pattern (moving bed, fluidized, or entrained bed). The proportions of the resulting product gases are determined by the type and composition of coal, the gasifying agent (or gasification medium), and the thermodynamics and chemistry of the gasification reactions as controlled by the process operating parameters. Coal gasification technology has the potential to be used in the following energy systems:

1. Fuel production for use in electric power generation units

2. Synthetic or substitute natural gas (SNG) production for pipeline gas supplies

3. Hydrogen production for fuel cell applications

4. Synthesis gas production for use as a chemical feedstock

5. Production of fuel gas (low or medium BTU gas) for industrial use

Coal is the most abundant recoverable fossil fuel resource in the United States and the world. Synthesis gas production is the starting point for the production of a wide range of chemicals. The success of the Tennessee Eastman Corp. in producing acetic anhydride from coal shows the great potential of using coal as petrochemical. feedstock.2 A major concern for such a technology involves the contaminants in coal.

Coal contains significant amounts of sulphur, which is of particular concern to downstream processes because many catalysts used in chemical production are highly susceptible to sulphur poisoning. Coals also contain trace amounts of alkali metal compounds, which contribute to the fouling and corrosion of reactor vessels as slag. Furthermore, coal contains a number of trace elements that may interfere with downstream processes and pose environmental and safety risks. If coal gasification is to be used to produce specific target chemicals, the choice of gasification technology is critical because a different process will produce a different quality (or composition) of synthesis gas as well as change the economics of production.

Synthesis gas (SG) is an essential raw material for both fuels and petrochemicals. Synthesis gas is also referred to as syn gas or syngas. It can be obtained from various sources including petroleum, natural gas, coal, biomass, and even municipal solid wastes (MSWs). Syngas is conveniently classified, based on its principal composition, as: (1) H2-rich gas, (2) CO-rich gas, (3) CO2-rich gas, (4) CH4-rich gas, etc. Principal fuels and chemicals directly made from syngas include hydrogen, carbon monoxide, methane, ammonia, methanol, dimethylether, gasoline, diesel fuel, ethylene, isobutylene, mixture of C2-C4 olefins, C1-C5 alcohols, ethanol, ethylene glycol, etc. 74

Secondary fuels and chemicals synthesised via methanol routes include formaldehyde, acetic acid, gasoline, diesel fuel, methyl formate, methyl acetate, acetaldehyde, acetic anhydride, vinyl acetate, dimethylether, ethylene, propylene, isobutylene, ethanol, C1-C5 alcohols, propionic acid, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), benzene, toluene, xylenes, ethyl acetate, a methylating agent, etc. The use of methanol as an intermediate in the synthesis of such chemicals is known as indirect synthesis.

Syngas Classification Based On Its Heating Value

Product gases are typically classified into three types of gas mixtures based on the heating values of the resultant synthesis gases produced by gasification processes:

1. Low-Btu gas consisting of a mixture of carbon monoxide, hydrogen, and some other gases with a heating value typically less than 300 Btu/scf.

2. Medium-Btu gas composed of methane, carbon monoxide, hydrogen, and various other gases with a heating value ranging from 300 to 700 Btu/scf.

3. High-Btu gas consisting predominantly of gases with a heating value of approximately 1000 Btu/scf. SNG is another name for it. Coal gasification is the process by which coal carbon (more precisely, macromolecular coal hydrocarbons) and other pyrolysis products react with oxygen, hydrogen, and water to produce fuel gases.

CHAPTER 2

CLASSIFICATION OF LOW-BTU GAS

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Product gases are typically classified as one of three types of gas mixtures based on the heating values of the resultant synthesis gases produced by gasification processes. Low-Btu gas containing of a mixture of carbon monoxide, hydrogen, and some other gases with a heating value typically less than 300 Btu/scf. Medium-Btu gas composed of a mixture of methane, carbon monoxide, hydrogen, and various other vapours with a heating value ranging from 300 to 700 Btu/scf. High-Btu gas consisting predominantly of gases with a heating value of approximately 1000 Btu/scf. It is also known as SNG. Coal gasification is the reaction of coal carbon (more precisely, macromolecular coal hydrocarbons) and other thermal decomposition products with oxygen, hydrogen, and water to produce fuel gases.

Medium-Btu Gas

Pure oxygen, rather than air, is used as the combusting agent in the production of medium-Btu gas, resulting in an appreciable increase in heating value of about 300-400 Btu/scf. The product gas consists primarily of carbon monoxide and hydrogen, with trace amounts of carbon dioxide as well as methane. It is primarily used in the Fischer-Tropsch synthesis of methanol, higher hydrocarbons, and a variety of other chemicals. It can also be used as a direct fuel source to generate steam or to power a gas turbine. In medium-Btu gas, the H2-to-CO ratio varies from 2:3 (CO-rich) to more than 3:1. (H2-rich). The higher heating value is attributed to higher methane and hydrogen contents, as well as lower carbon dioxide concentrations, and the utter lack of nitrogen in the gasifying agent.

High-Btu Gas

Because high-Btu gas is primarily composed of pure methane (>95%), its heating value ranges between 900 and 1000 Btu/scf. It is natural gas compatible and can be used as a synthetic or substitute natural gas (SNG). This type of syngas is typically produced through a catalytic reaction of hydrogen and carbon monoxide, which is known as the methanation reaction. Carbon dioxide and methane are usually present in trace amounts in the feed syngas. In addition, steam is typically present in the gas or added to the feed to reduce carbon fouling, which reduces catalytic effectiveness.

$$3H_2 + CO = CH_4 + H_2O$$
$$2H_2 + 2CO = CH_4 + CO_2$$

The first chemical reaction leading to methane is the most prevalent. The term "responsibility" refers to the act of determining whether or not a person is responsible for his or her own actions. The large amount of H2O produced is removed by condensation and recirculated as process water or steam. The majority of the exothermic heat generated by the methanation reaction is recovered during this process via a variety of energy integration processes.

While all of the reactions listed above are quite strongly exothermic with the exception of the forward water gas shift (WGS) reaction, which is mildly exothermic, the amount of CO present in the feed syngas has a large impact on heat release. An adiabatic retort will experience a 60°C temperature rise for every 1% CO in the feed syngas, which is known as adiabatic temperature rise.

Several metals have catalytic effects on the methanation reaction. Ru > Ni > Co > Fe > Mo in terms of catalytic activity. Because of its low cost and relatively high catalytic activity, nickel is by far the most widely used catalyst in commercial processes. Almost all commercially available catalysts used in this process, however, are very susceptible to sulphur poisoning, and all hydrogen sulphide (H_2S) must be removed before the catalytic reaction begins. To maintain adequate catalyst activity over a long period of time, the sulphur concentration in the feed gas must be reduced to less than 0.5 ppm. As a result, the catalyst development goal has been to improve the catalyst's sulphur tolerance.

Comflux, HICOM, and direct methanation are three notable commercial methanation processes. Comflux is a Ni-based, pressurised fluidized bed (PFB) process that converts CO-rich gases in and out of SNG in a single stage by combining methanation and WGS reactions. The British Gas Corporation's HICOM process is a fixed bed process that involves a series of methanation stages using syngas with a low H_2-to-CO ratio. The Gas Research Institute (GRI) developed a process that methanates equimolar mixtures of H_2 and CO, generating CO_2 rather than H2O (steam) in addition to methane:

$$2\ H_2 + 2\ CO = CH_4 + CO_2$$

It should be noted that the mechanistic chemistry discussed in this section is based on reactions between carbon and gaseous reactants, not coal and gaseous reactants. Even though carbon is the most abundant atomic species in coal, its reactivity differs significantly from that of coal or coal hydrocarbons. Coal is more reactive than pure carbon in general for a variety of reasons, including the presence of reactive organic functional groups and the availability of catalytic activity via naturally occurring nutrient ingredients. It may now be clear why anthracite, which has the highest carbon content of any coal rank, is the most difficult to gasify or liquefy. Alkali metal salts are known to catalyse the steam gasification reaction of activated carbon, including coals. The order of catalytic activity of alkali metals on coal gasification reaction is Cs > Rb > K > Na > Li. Carbon deposition reaction may affect catalyst life in the case of catalytic steam gasification of coal by fouling the catalyst active sites. The term "electronic commerce" refers to the sale of goods and services over the internet.

Carbon Dioxide Gasification

For modelling purposes, the reaction of coal with CO2 can be approximated or simplified as the initial response of carbon with carbon dioxide. The Boudouard reaction occurs when carbon dioxide reacts with carbon to produce carbon monoxide. This reaction, like the steam gasification reaction, is endothermic in nature. The reverse reaction is a carbon sworn testimony reaction that causes carbon fouling on many surfaces, including process catalyst deactivation. This gasification reaction is thermodynamically favoured at high temperatures ($T > 680°C$),which is also quite similar to the heat gasification. If carried out alone, the reaction requires high temperature (for a fast reaction) and high pressure (for higher reactant concentrations) to achieve significant conversion. However, in practical gasification applications, this reaction is almost never attempted as a single chemical reaction due to a variety of factors such as low conversion, slow kinetic rate, low thermal efficiency, unimpressive process economic history, and so on. Carbon monoxide slows the overall reaction rate in both mechanisms. In Mechanism A, carbon monoxide adsorption to free sites causes retardation, whereas in Mechanism B, chemisorbed oxygen reacts with gaseous carbon monoxide to produce gaseous carbon dioxide. As previously stated when discussing heat gasification, the CO_2 gasification rate of coal differs from the carbon-CO_2 rate for the same reason.

In general, the carbon-CO_2 reaction has a worldwide reaction order on the CO_2 partial pressure of one or less, i.e., 0.5 n 1, whereas the coal-CO_2 reaction follows a global reaction order on the CO_2 partial pressure of one or greater, i.e., 1 n 2. The observed higher reaction for the coal reacts is also due to the high reactivity of coal for the reasons.

Unlike the steam and CO_2 gasification reactions, this reaction is exothermic and thermodynamically favoured at low temperatures (T 670°C). At low temperatures, however, the reaction rate is invariably too slow. As a result, high temperature is always required for kinetic reasons, which in turn requires high hydrogn pressure, which is also preferred from an equilibrium standpoint. K_2CO_3, nickel, iron chlorides, iron sulphates, and other metals can catalyse this reaction. However, because of the low raw material value and the difficulty in recouping and reusing the catalyst, the use of catalyst in coal gasification faces serious economic constraints. As a result, catalytic coal biogas has not been widely used.

Coal combustion or oxidation is far more complicated than carbon oxidation. Coal is a multifunctional, probably the most iconic, heterogeneous macromolecule that occurs in a highly porous form (typical porosity of 0.3-0.5) with a very large available internal surface area (typically in the range of 250-700 m2/g). Coal's internal surface area is commonly expressed in terms of specific surface area, which is an intensive property that measures the individual surface area available per unit mass. The term "responsibility" refers to the act of determining whether or not a person is responsible for his or her own actions. Furthermore, transport processes of simultaneous heat and mass transfer complicate the reaction phenomenon. A variety of factors and operating parameters influence the overall rate of coal oxidation, both complete and partial, including reaction temperature, O2 partial pressure, coal porosity and distribution, coal particle size, coal types, types and contents of specific hematite, heat and mass transfer conditions in the reactor, and so on.

Kyotani et al. measured the reaction rate of combustion for five different coals over a wide temperature range of 500 to 1500°C to investigate the effects of coal rank (i.e., carbon content) and coal mineral matter catalysis. The combustion rates were correlated with various char characteristics based on their experimental results. It was discovered that the catalytic effect of mineral matter is a determining factor for coal reactivity in a region where chemical reaction rate controls the overall rate, i.e., typically in a low-temperature region where the kinetic rate is much slower than the diffusional rate of reactant. It was also found that for high-temperature regions where the external mass transfer rate controls the overall rate, the reactivity of coal decreased with increasing coal rank. The mechanistic rate of external mass transfer is the slowest of all mechanistic rates, including the surface reaction rate and the pore diffusional rate of reactant and product, when the external mass transfer rate limited (or controlled) the overall rate of reaction. This type of controlling regime is common in high-temperature operations because the intrinsic kinetic rate is far more strongly correlated with heat than the external mass transfer rate.

Water Gas Shift (Wgs) Reaction

Even though the WGS reaction is not one of the primary gasification reactions, it cannot be overlooked when analysing chemical reaction systems involving synthesis gas. This reaction equilibrium is the least sensitive to temperature variation of any reaction involving synthesis gas. In other words, its equilibrium constant is the least temperature dependent. As a result, this reaction equilibrium can be reversed in a wide range of practical process conditions and temperatures. WGS reaction in its forward path is mildly exothermic as:

$$CO\ (g) + H_2O\ (g) = CO_2\ (g) + H_2\ (g) \qquad \Delta H^\circ_{298} = -41.2\ \text{kJ/mol}$$

Despite the fact that all of the participating reactive species are in the form of a gas, scientists believe that this reaction takes place primarily at the heterogeneous surfaces of coal and is catalysed by carbon surfaces. Because the WGS reaction is catalysed by many heterogeneous surfaces and can occur both homogeneously and heterogeneously, achieving a generalised understanding of WGS reaction has been extremely difficult. Even kinetic rate data from the literature may not be immediately useful or appropriate to a real-world reactor situation.

Other than carbon monoxide and hydrogen, the syngas produced by a gasifier contains a variety of gaseous species. Carbon dioxide, methane, and water are common examples (steam). The structure of syngas may need to be preferentially readjusted depending on the process's goal. If the goal of the gasification is to obtain a high methane yield, the molar ratio of hydrogen to carbon monoxide should be set at 3:1, according to the methanation reaction stoichiometry

$$CO\ (g) + 3\ H_2\ (g) = CH_4\ (g) + H_2O\ (g)$$

If the goal of producing syngas is to produce methanol via a vapor-phase low-pressure process, the stoichiometrically coherent ratio of hydrogen to carbon monoxide would be 2:1. In such cases, the stoichiometrically consistent syngas mixture is often referred to as balanced gas, while a syngas composition that deviates significantly from the stoichiometry of the principal reaction is referred to as unbalanced gas. If the goal of syngas production is really to obtain a high hydrogen yield, it would be advantageous to increase the H_2 to CO ratio by further transforming CO (and H_2O) into H2 (and CO2) via the WGS reaction. However, if the final gaseous product is to be used in fuel cell applications, the carbon monoxide and carbon dioxide levels must be reduced to acceptable levels using a process including such acid gas removal or other adsorption processes.

Carbon monoxide and sulphurous species must be thoroughly removed from the hydrogen gas for hydrogen porous membrane (PEM) fuel cell operation. The WGS reaction is one of the major reactions in the steam gasification process, and it contains significant amounts of both water and carbon monoxide. Despite the fact that all four chemical species engaged in the WGS reaction are gaseous compounds at the reaction stage of most gas processing, the WGS reaction occurs predominantly heterogeneously, i.e. on the solid surface of coal, in the case of steam gasification of coal. If the product resulting in different from a gasifier needs to be reconditioned by the WGS reaction, a variety of metallic catalysts can be used to catalyse this reaction.

The type of catalyst used has always been determined by the desired outcome, the prevailing temperature conditions, the composition of the gas mixture, and the process economics. Many researchers have studied the WGS reaction using various catalysts such as iron, copper, zinc, nickel, chromium, and molybdenum. Significant effort has gone into developing a strong catalyst system with superior sulphur tolerance and a wider temperature range.

Syngas Generation Via Coal Gasification

The various types of synthesis gas were classified in the preceding section. Similarly, there are many different types of gasification processes. The gasification processes can be classified basically in three basic ways: (1) by the Btu content of the product gas,6 and (2) by the type of the reactor hardware configuration, as well as by whether the reactor system is operated under pressure or not. The following coal-to-gas conversion processes are classified based on the heating value of the product gas. Medium- or High-Btu Gas Gasification Processes:

1. Gasifier Lurgi
2. Gasifier for Synthane
3. molten iron coal gasifier Atgas

Processes for Gasification of Low- or Medium-Btu Gas

1. Gasifier Koppers-Totzek
2. The molten salt gasifier from Kellogg's
3. Gasification of CO2-acceptors
4. . U-gas procedure

Process of Gasification Using Only Low-BTU Gas

1. Process of underground in situ gasification

Gasification processes can also be classified into four types based on reactor configuration and method of contacting gaseous and solid streams:

2. Fixed or portable bed: In the fixed bed reactor, coal is supported by a grate and the gasifying media (steam, air, or oxygen) pass upward through the supported bed, whereby the product gases exit from top of the reactor.

The fixed bed reactor can only use noncaking coals. In the moving bed reactor, on the other hand, coal and gaseous streams move countercurrently, i.e., coal moves downward by gravity while gas moves upward through the coal bed. The bottom of the reactor has a higher temperature than the top. Because of the lower temperature at the top for coal devolatilization, this type of gasifier produces a large amount of liquid hydrocarbons. The residence time of the coal in both types of reactors is much longer than in a suspension reactor, allowing for ample contact time between reactants. Ash is removed from the reactor's bottom as dry ash or slag. This type of reactor includes Lurgi and Wellman-Galusha gasifiers. It should be clear that a moving bed reactor is a type of fixed bed reactor because the solids in the bed remain together irrespective of the movement of the hardware that supports the bed.

Fluidized bed: This method employs finely pulverised coal particles. The term "independent" refers to a person who does not work for the government. Because of the ascent of particles and fluidizing gas, more coal surface area is made available, which promotes the gas-solid chemical reaction, resulting in increased carbon conversion. This type of reactor allows for close contact between gas and solid coal fines while also providing longer residence times than an entrained flow reactor. Dry ash is either continuously removed from the bed or the gasifier is operated at such a high temperature that agglomerates can be removed. Due to operational complications throughout fluidization characteristics, such beds have a limited ability to handle caking coals.

This reactor is used in the Winkler and Synthane processes. The term "responsibility" refers to the act of determining whether or not a person is responsible for his or her own actions. This reactor system employs finely pulverised coal particles blown through into gas stream prior to reactor entry, with combustion and gasification taking place within the coal particles suspended in the gas phase. Because of the entrainment requirement, high gas stream space velocity and fine powdery coal particles are critical to the operation of this type of process. Because of the reactor's extremely short residence time (i.e., high space velocity), a very high temperature is required to achieve good conversion in such a short period of reaction time.

This can also be aided by the use of extra oxygen. This bed configuration is typically capable of handling both caking and noncaking coals with little difficulty. Examples of commercial gasifiers that use this type of reactor include the Koppers-Totzek gasifier and Texaco gasifier. Molten salt bath nuclear power plant: In this reactor, coal is fed along with steam or oxygen in the molten bath of salt or metal operated at 1,000-1,400ºC. As slag, ash and sulphur are removed. This reactor is used in the Kellogg and Atgas processes.

General Aspects Of Gasification

Temperature, pressure, gas composition, and the nature of the coal being gasified all influence the kinetic rates and extents of conversion for various gasification reactions. The rate of reaction is intrinsically higher at higher temperatures, whereas the equilibrium of the reaction may be favoured at either higher or lower temperatures depending on the specific type of gasification reaction. The effect of pressure on the rate also depends on the specific reaction. Thermodynamically, some gasification reactions including carbon-hydrogen reaction producing methane are favored at high pressures (>70 atm) and relatively lower temperatures (760-930°C), whereas low pressures and high temperatures favour the production of syngas (i.e., carbon monoxide and hydrogen) via steam or carbon dioxide gasification reaction.

In terms of economics, design, and operability, heat supply and recovery are critical components of the gasification process. The partial oxidation of char with steam and oxygen produces heat and synthesis gas. The cyclic reduction and oxidation of iron ore is another method for producing a hot gas stream. The type of coal used in gasification is also important for gasification and downstream operations. Only suspension-type gasifiers, such as the entrained flow reactor, can handle any type of coal; however, if caking coals are to be used in a fixed or fluidized bed, special precautions must be taken to prevent coal agglomeration (or cake) during gasification. If such agglomeration occurs, it will have a negative impact on the gasification process's operability. Furthermore, the chemical composition, volatile matter (VM), and moisture content of coal all play important roles in coal processing during gasification. The S and N contents of coal have a significant impact on the quality of the product gas as well as the requirements for gas cleaning. The sulphur content of coal typically comes from three different sources of coal sulphur, namely, pyritic sulphur, organic sulphur, and sulfatic sulphur.

The first two sulphur forms are more dominant, whereas weathered or oxidised coals have more sulfatic forms than fresh coals. Depending on the nature of the reactive environment, sulphur dioxide gas species can be sulphur dioxide, hydrogen sulphide, or mercaptans. Sulfur dioxide serves as the dominant sulfur-containing species in the product gas if the reactive environment is oxidative.

Lurgi Gasification

The Lurgi gasifier is one of several that have fully developed commercial technology. Since its development in Germany before World War II, this process has been used in a large number of commercial plants throughout the world. As a byproduct, this process generates low- to medium-Btu gas. It is a fixed bed process because the reactor configuration is similar to that of a typical fixed bed reactor. The older Lurgi process is a dry ash gasification process, which is very different from the more recently developed slagging gasifier. The Lurgi dry ash gasifier is a pressurised vertical reactor that only accepts crushed noncaking coals. The coal feed is supported at the base of the reactor by a revolving grate through which the steam and oxygen mixture is introduced and the ash removed. This process occurs at a pressure of 24 to 31 atm and a temperature of 620 to 760°C. The residence time in the reactor is approximately 1 hour. The hydrogen species is supplied by steam introduced from the reactor's bottom, and the heat is supplied by the combustion of a portion of the char. When compared to a nonpressurized gasifier, the product gas from a greater reactor has a relatively high methane content. The high methane content of the product gas is a result of the relatively low gasification temperature. If oxygen is used as an injecting (and gasifying) medium, the exiting gas has a heating value of approximately 450 Btu/scf. The crude gas exiting the gasifier contains a significant amount of condensable products such as tar, oil, phenol, and so on, which are separated in a devolatilizer, which cleans the gas to remove unsaturated hydrogen and naphtha. The gas is then methanated ($CO + 3H_2 = CH_4 + H_2O$) to create a high-Btu gas (pipeline quality).

The gasifier shell is water-cooled, and the water jacket generates steam.

At the top of the coal sleep, a motor-driven distributor distributes the feed coal from the coal lock hopper evenly. A motor drives the grate at the bottom of the reactor to discharge the coal ash into the ash lock hopper. There are several distinct zones between the inlet and outlet grates. The topmost zone preheats the feed coal by contacting it with hot, ready-to-exit crude product gas. Devolatilization and gasification reactions occur at temperatures ranging from 620 to 760°C as the coal is heated. The gasification of the resulting char is accompanied by the devolatilization of coal. The interaction between devolatilization and gasification is a determining factor in the process kinetics and product compositions.

The combustion zone is at the bottom of the bed, where coal carbon reacts with oxygen to produce primarily carbon dioxide. This reaction generates exothermic heat, which is used to heat gasification and devolatilization, both of which are endothermic reactions. Energy integration within the gasifier is accomplished by utilising the exothermic heat of combustion in the gasification and devolatilization, both of which are endothermic. More than 80% of coal fed is gasified, with the remainder burned in the combustion zone. Sacrificial coal is the portion of feed coal burned for in situ heat generation.

The combustion zone temperature must be chosen so that it is below the ash fusion point but high enough to ensure complete gasification of coal in subsequent zones. The steam-to-oxygen ratio also influences this temperature. The following process variables influence the Lurgi gasifier's material and energy balance:

1. Pressure, temperature, and the ratio of steam to oxygen.

2. The nature of the gasification and devolatilization reactions is determined by the type of coal used. Lignite is the most reactive coal, with a reaction temperature of 650°C. Coke, on the other hand, is the least reactive, with a minimum temperature for chemical reaction of around 840°C. As a result, lignite gasifies more coal per unit mole of oxygen than other types (ranks) of coal. The lower the coal reactivity, the higher the coal rank (i.e., the carbon content of coal).

3. The coal's ash fusion point, which limits the maximum operable temperature in the combustion zone and thus determines the steam-to-oxygen ratio.

4. The amount and chemical composition of coal's volatile matter, which affects the quality and quantity of tar and oils produced.

Because of its medium-pressure operation and countercurrent gas-solid flow, the Lurgi gasifier has a relatively high thermal efficiency. At the same time, it consumes a lot of steam and has a high carbon dioxide concentration in the crude product gas. Furthermore, the crude gas exiting the gasifier contains a significant amount of carbonization products such as tar, oil, naphtha, ammonia, and so on. Devolatilization, pyrolytic reactions, and secondary chemical reactions involving intermediates produce these carbonization products. This crude product gas is washed and cooled by a waste heat boiler after passing through a scrubber.

Koppers-Totzek Gasification

This gasification process employs entrained flow technology, in which finely pulverised coal is mixed with steam and oxygen and fed into the reactor. 14,15 Atmospheric pressure is used in the process. The space time in the reactor is very short, as with all encapsulated flow reactors. The gasifier is a refractory-lined cylindrical coal burner with at least two burner heads that charge coal, oxygen, and steam.

The burner heads are spaced 180° apart (for two-headed designs) or 90° apart (for four-headed designs) and are designed so that steam covers the flame and prevents the reactor refractory walls from becoming too hot. The reactor typically operates at around 1400-1500°C and atmospheric pressure. The reaction rate of gasification is especially high at this high temperature, orders of magnitude higher than at a temperature in a typical fixed bed reactor. Depending on the type of coal, about 90% of carbonaceous matter is gasified in a single pass.

Lignite is the most reactive coal, with a reactivity that approaches 100%. Unlike moving bed or fluidized bed reactors, this gasifier has few restrictions on the caking behaviour and mineral matter (ash) properties of the feed coal. Because of the extremely high temperatures of operation, the ash agglomerates and falls out of the combustion zone as molten slag, eventually being removed from the reactor's bottom.

Hot effluent gases are cooled and cleaned. This gas product is primarily synthesis gas and contains neither any tar, ammonia, or condensable hydrocarbons. It has a heating value of approximately 280 Btu/scf and can be upgraded further by reacting with steam to form complex hydrogen and carbon dioxide via the WGS reaction (Figure 2.1).

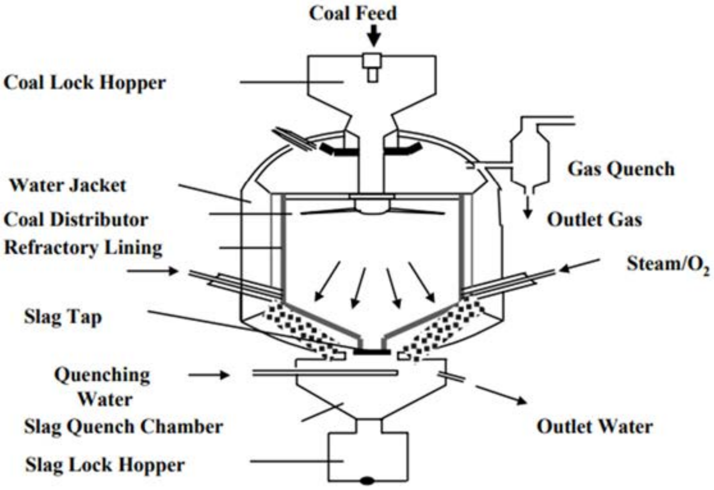

Figure 2.1 represent the f slagging Lurgi gasifier.

The atmospheric pressure. The space time in the reactor is very short, as with all entrained flow reactors. The gasifier is a refractory-lined cylindrical coal burner with at least two heating heads that charge coal, oxygen, and steam. The burner heads are spaced 180° apart (for two-headed designs) or 90° apart (for four-headed designs) and are designed so that steam covers the flame and prevents the reactor refractory walls from becoming too hot. The reactor typically operates at around 1400-1500°C and atmospheric pressure. The reaction rate of gasification is extremely high at this high temperature, orders of magnitude higher than at a temperature in a typical fixed bed reactor. Depending on the type of coal, about 90% of carbonaceous matter is gasified in a single pass. Lignite is the most reactive coal, with a reactivity that approaches 100%. Unlike moving bed or fluidized bed reactors, this gasifier has few restrictions on the caking behaviour and mineral matter (ash) properties of the feed coal. Because of the extremely high operating temperatures, the ash agglomerates and falls out of the combustion zone as molten slag, eventually being removed from the reactor's bottom. Hot effluent gases are cooled and cleaned.

This gas product is primarily synthesis gas and contains no tar, ammonia, or condensable hydrocarbons. It has a heating value of approximately 280 Btu/scf and can be upgraded further by reacting with water to form additional hydrogen and carbon dioxide via the WGS reaction. Gaseous and vapour hydrocarbons emitted by coal at a moderate temperature are passed through a zone of extremely high temperature, where they decompose so quickly that no coal particles coagulate during the plastic stage. Thus, Any coal, regardless of caking real estate, ash content, or ash fusion temperature, can be gasified. The reactor temperature drops from 1930°C (flame temperature) to 1500°C as a result of endothermic reactions between carbon and steam in the gasifier and radiation to the refractory walls. Only gaseous products are formed under these conditions, with no tars, condensable hydrocarbons, or phenols formed. The following are typical assemblies of Koppers-Totzek gaseous products:

In the high-temperature zone, the ash in the coal feed becomes molten. Approximately half of the coal ash is discharged as slag into a slag quench tank beneath the gasifier. The remaining ash exits the gasifier as fine fly ash. Water sprayers are installed at the gasifier outlet to lower the gas temperature below the ash fusion temperature. This cooling keeps slag particles from adhering to the waste heat boiler tubes, which are mounted above the gasifier.

The raw gas from the gasifier is routed through to the waste heat boiler, which generates high-pressure steam up to 100 atm via waste heat recovery. After exiting the waste heat boiler, the gas is cleaned and cooled in a highly efficient scrubbing system, which reduces entrained solids to 0.002-0.005 grains/scf or less and lowers the temperature from 175 to 35°C. Electrostatic precipitators (ESPs) are used to clean the gas produced by the Koppers-Totzek process before it is compressed to high pressures for chemical synthesis. Several gasifiers can share cleanup and cooling equipment, lowering capital costs.

CHAPTER 3

SHELL GASIFICATION

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The Shell coal gasification process was developed in the early 1970s by the Royal Dutch and Shell groups. It uses a pressurised, slagging-entrained flow reactor to gasify dry pulverised coal. 19 It, like the Koppers-Totzek process, has the potential to gasify a wide range of coal ranks, including low-rank lignites with high moisture content. Unlike other gasifying processes, it uses pure oxygen as the gasifying medium for partial oxidation gasification. Shell Global Solutions licences two versions of gasification technologies, one for liquid feedstock applications and the other for coal and petroleum coke.. The following characteristics are present in the procedure:

1. Conversion of nearly all coals, including high-sulfur coals, lignites, and coal fines, to nearly 100%.

High thermal efficiency in the 75-80% range

3. Efficient heat recovery via high-pressure superheated steam production

4. Production of clean gas with no significant by-products

5. Fast throughput

6. Environmental friendliness

Before being fed into the gasifier vessel, the coal is crushed and ground to less than 90-m size. This pulverised and dried coal is introduced into the reaction chamber via diametrically opposed diffuser guns. 21 The coal is then reacted with pure oxygen and steam, with the flame temperature reaching 1800-2000°C. A typical operating pressure is around 30 atm. The raw product gas is typically composed primarily of carbon monoxide (62-%) and hydrogen (28%), with trace amounts of carbon dioxide.

Molten ash is collected in a water-filled bottom compartment. Some ash is entrained with the synthesis gas and recycled with the unconverted carbon. A quench section is provided at the reactor outlet to reduce the temperature of the gas. The removal of particulate matter from raw product gas is inte6rated into the overall process. This removal system is typically comprised of cyclones and scrubbers. The main advantage of this section is the elimination of solid-containing wastewater, which eliminates the need for filtration.

Texaco Gasification6

The Texaco process also employs entrained diffusion technology for coal gasification. It gasifies coal under relatively high pressure by injecting oxygen (or air) and steam while simultaneously flowing gas and solid. To create a pumpable slurry, fluidized coal is mixed with either oil or water. This slurry is circulated under pressure into a vertical gasifier, which is essentially a pressure vessel with refractory walls on the inside. At high temperatures, the slurry reacts with either air or oxygen. The product gas is primarily composed of carbon monoxide, carbon dioxide, and hydrogen, with a trace of methane. Oil or tar are not produced due to the high temperature. This process is primarily used to produce CO-rich synthesis gas.

The Texaco partial oxidation process, used to gasify crude oil and hydrocarbons, was the inspiration for this gasifier. The use of coal slurry feed simplifies the coal-feeding system and the operability of the gasifier. The gasifier is a straightforward vertical, cylindrical pressure vessel with refractory linings in the partial oxidation chamber. It also has a slag quench zone at the bottom to cool down the resultant gases and molten slag. Large amounts of high-pressure steam can be obtained in the latter operation, increasing the thermal efficiency of the process. The water content of the coal slurry is another important factor influencing gasifier thermal efficiency. This water content should be kept as low as possible because a large amount of oxygen is required to provide the heat required to vaporise the slurry water. This gasifier prefers high-energy dense coals, resulting in a low water-to-energy ratio in the feed. As a result, bituminous coals from the eastern United States are preferable to lignites for this gasifier. The gasifier operates at temperatures ranging from 1100 to 1370°C and pressures ranging from 20 to 85 atm.

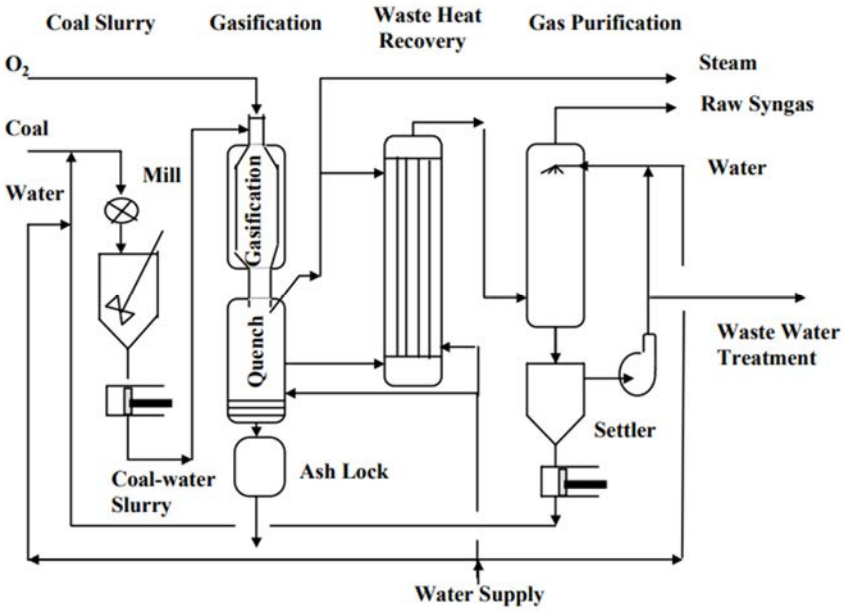

Figure 3.1 represent the Texaco gasification process.

The reaction zone's product gases and molten slag pass downward through a water spray chamber and a slag quench bath, where the cooled gas and slag are removed for further treatment. After being separated from the slag and cooled, the gas is treated to remove carbon fines and ash. While the cooled gas is treated for acid gas removal and elemental sulphur is recovered from the hydrogen sulphide (H_2S)-rich stream, the fines are recycled to the slurry preparation system.

In Situ Gasification

In situ gasification, also known as underground synthesis gas, is a technology for recovering the energy content of coal deposits that cannot be economically or technically exploited using traditional mining (or ex situ) processes. Low heating values, thin seam thickness, great depth, high ash or excessive moisture content, large seam dip angle, or undesirable overburden properties characterise coal reserves that are suitable for in situ gasification. Underground coal gasification (UCG) has been studied extensively in the former Soviet Union and Australia, but it is only recently that the concept has been resurrected in Europe and North America as a means of producing fuel gas.

Aside from the possibility of recovering deep, low-rank coal reserves, the UCG process may have some advantages in terms of resource recovery, a small ecological footprint, operational safety, process efficiency, and economic potential. The goal of in situ coal gasification is to convert petroleum hydrocarbons into combustible gases via coal seam combustion in the presence of air, oxygen, or steam.

The combustion process could be carried out in either forward or reverse mode. Forward combustion occurs when the combustion front and injected air both move in the same direction, whereas reverse combustion occurs when the combustion front moves in the opposite direction as the injected air.

The procedure entails drilling and then connecting the two boreholes to allow gas flow between them. Combustion begins at the bottom of a single borehole known as an injection well and is sustained by the continuous injection of air.

As shown in Figure 3.2 , carbon dioxide is produced in the initial reaction zone by the reaction of oxygen (air) with coal, which then reacts with coal to produce carbon monoxide in the reduction zone via the Boudouard reaction ($CO_2 + C = 2CO$). Furthermore, at such high temperatures, moisture in the seam may react with carbon to produce carbon monoxide and hydrogen via the steam gasification reaction ($C + H_2O = CO + H_2$).

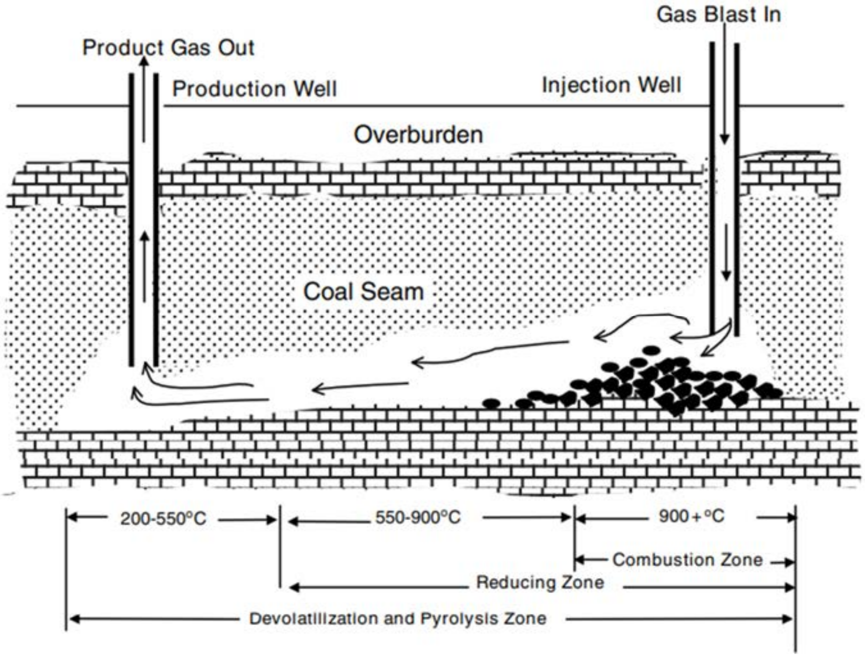

Figure 3.2 represent the situ underground gasification process.

In addition to all of these fundamental gasification reactions, coal decomposes in the pyrolysis zone due to high temperatures, producing hydrocarbons and tars that contribute to the product gas mix. The heating value of the in situ air-blown gasifier is approximately 100 Btu/scf. The low heat content of the gas makes transportation uneconomical, necessitating the use of the product gas on-site. Thompson and Gregg and Edgar's references provide extensive discussion of in situ gasification.

The Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia has also made significant R&D efforts in underground coal gasification. Researchers at CSIRO have created a model to aid in the deployment of this technology. Other trials and trial schemes were evaluated in Europe, China, India, South Africa, and the United States.

Potential Possibility of Using Microbial Processes For In Situ Gasification

Microorganisms that grow solely on coal have been discovered. Both organic and inorganic sulphur (pyritic and sulfatic) are claimed to be removable by biochemical techniques, and microorganisms can grow in solids with narrow pore structures. Large-molecular-weight aromatics, including polynuclear aromatics (PNAs), could also be converted. Knowledge of coal properties, both physical and chemical, under current conditions is an important prerequisite for developing such new process techniques for in situ coal converter in deep seams. The permeability of the coal seam, including the overburden, and the rank of coal are the two most important coal properties that govern in situ processes. Microporosity is an important parameter for microbial coal conversion. Because of the high rock overburden pressure, the permeability of coal seams at great depths is typically quite low. However, accessibility is critical for performing in-place processes. There are several methods for increasing the permeability of deep coal seams.

The primary advantage of using pathogens techniques is that the reaction occurs at room temperature. The development of these types of processes has made significant progress. The microorganisms can penetrate fine pores in the coal matrix and create new pores if substances in the coal matrix are converted into gaseous compounds, which is a remarkable effect of such reactions in coal. The transition from solely oxidative processes to methane-forming reactions, however, is the most difficult and complex problem associated with microorganism-based reactions. At least three reaction steps are involved: (1) aerobic coal degradation to biomass and high-molecular-weight products, (2) anaerobic coal degradation to acetate, hydrogen, and carbon monoxide, and (3) conversion of these products to methane using methanogenic bacteria. Archaea are primitive microorganisms that include methanogenic bacteria. They produce methane gas as a byproduct of metabolism and are frequent in sewage treatment plants and hot springs where the temperature is high and oxygen is scarce. Lower conversion temperatures and more valuable products are advantages of these processes over other conversion processes. However, extensive research is required to adapt reaction conditions and product yields to the conditions found in deep coal seams, where pathways play a significant role in the overall reaction.

Underground Gasification System

The underground gasification system is comprised of three distinct sets of operations: pregasification, syngas, and subsequent processing and utilisation. Pregasification operations allow access to and preparation of the coal deposit for gasification. Shafts and boreholes are used to connect the inlet and outlet through the coal seam. Pneumatic, hydraulic, or electric linking, as well as the use of explosives, are all methods of linking. Partially linking can also be accomplished by taking advantage of the coal seam's natural permeability. Only directionally drilled boreholes provide positive connections between inlet and outlet sections, while all other methods allow for some degree of uncertainty to play a role in the system. v a schematic view of a connected underground gasification plant near Moscow.

Gasification operations that allow for consistent production of low-Btu gas include the addition of gasifying agents such as air or oxygen and steam (or alternating air and steam), followed by ignition. Ignition can be controlled electrically or by burning solid fuels. At the flame front, contact between gasifying agents and coal organics occurs. The flame front may advance in the direction of gas flow (forward burning) or in the opposite direction of gas flow (reverse burning) (backward burning).

The major technical difficulties and challenges during these operations are in the area of process control. Because of the unique nature of underground gasification, there are inherent controllability and observability issues.

The next and most important operation is the use of the product gas, which necessitates a connection between the gas source and the energy demand. The product gas can be used to generate electricity on-site, or it can be upgraded to a high-Btu pipeline-quality gas for transmission. It could also be used as a hydrogen source, a reducing agent, or a basic raw material in the manufacture of other chemicals near the deposit. With the development of the hydrogen economy, product gas may have a high potential as a hydrogen source. Apart from potential environmental concerns, there are no major technical issues associated with the use of product gas.

Winkler Process

This is the first commercial process that makes use of fluidized bed technology. The method was invented in Europe in the 1920s. There are currently more than 15 plants in operation around the world, with the largest producing 1.1 million scf/d. Pulverized coal is dried and fed into a fluidized bed reactor via a variable speed screw feeder in this process. The gasifier operates at atmospheric pressure and temperatures ranging from 815°C to 1000°C. Coal particles react with oxygen and steam to produce carbon monoxide and hydrogen-rich offgas. Because of the relatively high operating temperature, the product gas stream contains very little tar and liquid hydrocarbons. Water scrubbers, cyclones, and electrostatic precipitators clean the gas stream, which can carry up to 70% of the generated ash (ESPs). Unreacted char carried over by the fluidizing gas stream is converted further in the space above the fluidized bed by secondary steam and oxygen. As a result, the highest temperature is found above the fluidized bed.

Gas is cooled by a radiant boiler before leaving the gasifier to prevent ash fines from melting at high temperatures and forming deposits in the exit duct. A waste heat recovery section is used to recycle the raw hot gas that exits the gasifier. The gas is then compressed and subjected to the WGS reaction. The heating value of the product gas is approximately 275 Btu/scf. The process's thermal efficiency is approximately 75%.Carbon was used instead of coal in the preceding reactions solely for illustration purposes. As a result, the actual reactions in the gasifier are far more complicated.

Because of the process's relatively high temperatures, nearly all of the tars and heavy hydrocarbons are reacted. As a result of fluidization, ash particles are separated based on particle size and specific gravity. About 30% of the ash falls to the ground, while 70% is carried overhead. The lighter particles carried upward by the produced gas are gasified further in the space above the bed. As a result, the amount of gasifying medium injected into this bed must be proportional to the amount of unreacted carbon carried over. If it is too low, ungasified carbon is carried out of the generator, resulting in a slightly lower thermal efficiency; if it is too high, product gas is consumed by combustion unnecessarily. Because of this secondary (further) gasification, the maximum temperature in the generator occurs in the space above the fluidized bed.

Before leaving the generator, a radiant boiler installed directly above the bed cools the hot product gas to 150-205°C. This helps to keep fly ash from sintering on the refractory walls of the exit duct. As an energy integration scheme, the sensible heat recovered by the radiant boiler generates superheated steam, which is used to preheat the boiler feed water (BFW). the typical gas composition of a Winkler gasifier. The data show that the product gas is high in carbon monoxide, resulting in a CO-rich syngas.

Wellman-Galusha Process

This method has been in advert use for over 40 years. It can generate low-Btu gas by using air (as a gasifying medium) for fuel gas or oxygen (as a gasifying medium) for synthesis gas. For this process, there are two types of gasifiers: standard without agitator and modified with agitator. The rated capacity of an agitated type gasifier is approximately 25% greater than that of a standard type gasifier of the same size. The agitated type can handle volatile caking bituminous coals, whereas the nonagitated type would struggle with this type of coal. Figure 3.3 depicts a schematic of a Wellman-Galusha agitated gasifier.

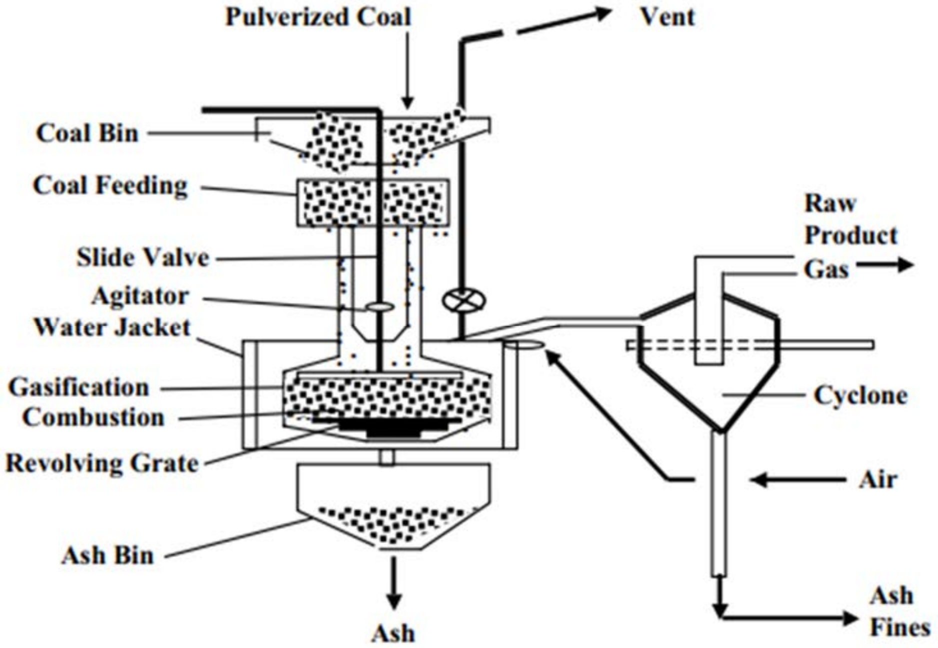

Figure 3.3 Represent the Wellman-Galusha gasifier.

This gasifier could be classified as either a fixed bed or a moving bed reactor. Because the gasifier shell is water-jacketed, the inner wall of the reactor vessel does not need a refractory lining. The gasifier runs at 540-650°C and atmospheric pressure. Pulverized coal is fed into the gasifier from the top via a lock hopper and vertical feed pipes, while steam and oxygen are injected through tuyeres at the bed's bottom. The fuel valves are operated to maintain a constant flow of coal to the gasifier, which also aids in bed stabilisation and thus product gas quality. The injected air or oxygen passes out over water jacket, producing the necessary steam for the process. A rotating grate at the gasifier's bottom removes ash from the bed uniformly. Under the grate, an air-steam mixture is introduced and evenly distributed through the pit into the bed. This gasifying medium undergoes a variety of chemical reactions as it passes through the ash, combustion, and gasifying zones in this specific order. If air is used as an injecting medium, the product gas contains hydrogen, monoxide, carbon dioxide, and nitrogen.

Before leaving the gasifier, the hot coal dries and preheats the incoming coal. A typical Wellman-Galusha gasifier product composition. The product gas is passed through a cylinder, which removes char particles and fine ash. It is then cooled and scrubbed in a clear countercurrent water cooler before being treated to remove sulphur. Because of the presence of a large amount of nitrogen, low-Btu gas is produced when air is used as an oxidant, whereas medium-Btu gas is produced when oxygen is used. The agitated Wellman-Galusha gasifier, as opposed to the standard Wellman-Galusha gasifier, has a slowly revolving horizontal neck that spirals vertically beneath the surface of the coal bed to minimise channelling. This arm also contributes to a uniform bed for gasification.

The U-GAS Process

The Institute of Gas Technology (IGT), Des Plaines, IL, developed the process to produce gaseous product from coal inside of an efficient and environmentally acceptable manner. The product gas can be used to generate low-Btu gas, medium-Btu gas, and SNG for use as fuels, and as chemical feedstocks for ammonia, methanol, hydrogen, oxo-chemicals, and so on, or to generate electricity via an IGCC. According to extensive research and pilot plant testing, the process is capable of handling large volumes of gas processing capacity, achieving a high conversion of coal to gas without producing tar or oil, and causing minimal environmental damage.

to keep ash from sagging. The pressure can be variable, typically ranging from 50 to 350 psi, and is largely determined by the final application of the product gas. Air can be used in place of oxygen. Coal is rapidly gasified in the gasifier, producing H_2, CO, CO_2, and trace amounts of CH4. Because the fluidized bed is always kept under reducing conditions, all sulphur species present in coal are converted into H2S. Concurrently with gasification, the ash is agglomerated into spherical particles that grow in size and are separated from the bed into water-filled ash hoppers, from which slurry is withdrawn. A portion of the fluidizing gas enters the gasifier section via an inclined grid, while the majority of the remaining entering gas flows rapidly upward through the ash-agglomerating zone, forming a relatively hot zone within the bed.

Two external cyclones collect coal fines elutriated from the bed. The first cyclone's fines are returned to the bed, while the second cyclone's fines are sent to the ash-agglomerating zone. Because raw product gas is virtually free of tar and oils, the subsequent energy recovery and gas purification steps are simplified. The IGT pilot plant has a gasifier made of a mild-steel, refractory-lined vessel with an I.D. of 3 ft. and a height of approximately 30 ft. Tampella Power Company, Finland, which later became Carbona Inc., developed an IGCC process based on the IGT U-GAS process. The IGT process was chosen because of its excellent carbon conversion and versatility with a wide range of coals and peat. Enviropower Inc. acquired the U-gas technology and renamed it Enviropower gasification technology. Carbona Inc. later purchased Enviropower's gasification business.

Catalytic Coal Gasification

Catalytic gasification has gotten a lot of attention in recent years because it uses less thermal energy but converts more carbon. Catalysis of coal gasification research has two goals: (1) to understand the kinetics of coal gasification involving active mineral matter, and (2) to design possible processes using these catalysts. Catalysts lower the gasification temperature, promoting product composition under equilibrium conditions as well as high thermal efficiency. However, unless the catalyst is relatively inexpensive or highly active at low temperatures, a catalytic process cannot compete with a noncatalytic one under normal conditions. Because of the high cost of separation and the low cost of coal and coal gas, recovering and reusing catalyst in the process is undesirable and unattractive in coal gasification. Catalysis research is divided into three categories: basic chemistry, application-related problems, and process engineering. Juntgen30 published a comprehensive review of catalytic gasification.

Nishiyama31 also printed a review article outlining some options for a well-defined catalytic research effort. The following observations are included in the article: Alkali and alkaline earth metal salts, as well as transition metals, are active gasification catalysts. The activity of a specific catalyst is affected by both the gasifying agent and the gasifying conditions. The main mechanism of alkali and alkaline earth metal salt catalysis in steam and carbon dioxide gasification involves the transfer of oxygen from the catalyst to carbon via the formation and decomposition of the C-O complex, i.e., C-O complex formation and decomposition (O).

The mechanism of iron or nickel-catalyzed hydrogasification reactions is still unclear. However, one possible explanation is that the active catalyst appears to be in a metallic state, and the mechanism consists of two major steps. These are hydrogen dissociation and carbon activation, respectively. Carbon dissolution into and diffusion through a catalyst particle appears logical in the latter case. Gasification occurs in two stages, each with its own temperature range and thermal behaviour, so a single mechanism cannot account for the entire reaction. As a result, it is still assumed that the catalyst will activate the hydrogen. This catalyst has a very high activity in the beginning when it is well dispersed in the other promoter catalyst, but as conversion increases, the activity decreases. Chemisorption of carbon dioxide, x-ray diffraction (XRD), and other analytical techniques are used to investigate the chemical state and dispersion. They verified the existence.

In comparison to other heterogeneous catalytic systems, gasification catalysis is complex because the catalyst is very short-lived and effective only while in contact with the substrate, which changes throughout the process. As a result, the definition of activity for such systems is not simple. The rate of an alkali metal catalyst increases due to changes in catalyst dispersion as well as an increase in the catalyst/carbon ratio in the later stages of gasification. Other explanations for the rate increase include changes in surface area caused by pore opening and changes in the chemical state of the catalyst. At the same time, some changes deactivate the catalyst, such as catalyst particle agglomeration, coking, and chemical reactions with sulphur or other trace elements.

Coking causes fouling on the catalyst surface as well as sintering, whereas sulphur reaction poisons the catalytic activity. The catalyst's activity is also affected by the nature of the substrate and the gasifying conditions. The main substrate properties related to activity are: (1) reactivity of carbonaceous constituents, (2) catalytic effect of minerals, and (3) effect of minerals on the activity of added catalyst. In terms of the factors influencing catalyst activity, the following general trends have been observed:

1. Nickel catalysts are more effective on lower-rank coals because they can be dispersed more easily into the coal matrix due to the higher permeability of the coal, whereas potassium catalyst efficiency is independent of rank. In any case, the carbon content of the coal alone cannot predict catalyst activity.

2. The internal surface area of coal char is related to the catalyst's overall activity. When the amount of catalyst is sufficient to cover the available surface area, it can be related to the number of active sites. The conversion of an immobile catalyst is nearly proportional to the initial surface area.

3. Pretreatment of coal prior to the catalytic reaction frequently aids in the achievement of higher reaction rates. Although coal pretreatment may not be directly applicable as a practical process, a suitable selection of coal types or processing methods may improve catalyst activity.

4. Coal mineral matter has a dual effect on catalyst effectiveness. Some minerals catalyse the reaction, such as alkali and alkaline-earth metals, whereas others, such as silica and alumina, interact with the catalyst and deactivate it. Demineralization generally increases the activity of potassium catalysts, but only slightly for calcium and nickel catalysts.

The method of loading the catalyst is also important for activity management. The catalyst should be loaded in such a way that there is definite contact between solid and gaseous reactants. When the catalyst was loaded from an aqueous, a hydrophobic carbon surface was observed.

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Coking fouls the catalyst surface and sinters it, whereas sulphur reaction poisons the catalytic activity. The activity of the catalyst is also affected by the nature of the substrate and the gasifying conditions. The main properties of the substrate related to activity are: (1) reactivity of the carbonaceous constituents, (2) catalytic effect of minerals, and (3) effect of minerals on the activity of added catalyst. In terms of factors influencing catalyst activity, the following general trends have been observed:

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3. Pretreatment of coal prior to the catalytic reaction frequently aids in achieving higher reaction rates. Although coal pretreatment may not be directly applicable as a practical process, a suitable selection of coal types or processing methods may increase the activity of catalysts.

4. The effect of coal mineral matter on catalyst effectiveness is twofold.

Some minerals, such as alkali and alkaline-earth metals, catalyse the reaction, whereas others, such as silica and alumina, interact with the catalyst and deactivate it. Demineralization generally increases the activity of potassium catalysts but only slightly for calcium and nickel catalysts.

The method of catalyst loading is also important for activity management. The catalyst should be loaded in such a way that there is definite contact between both solid and gaseous reactants.When the catalyst was loaded from an aqueous solution, a hydrophobic carbon surface reacted. Zinc oxides, like magnesium, have been shown to significantly accelerate gasification rates by 20-30%.

Murlidhara and Seras54 proposed some speculative mechanisms for the role of calcium oxide in increasing reaction rate. For example, coal organic matter may act as a donor of hydrogen, which is then abstracted by calcium oxide via the mechanism described in Scheme 1. The mechanism of generating oxygen-adsorbed CaO sites and subsequent elution of nascent oxygen, which reacts with organic carbon in coal to form carbon monoxide, is explained in Scheme 2. The third scheme explains the direct interaction between CaO and coal organics, which results in the release of carbon monoxide. The scheme goes on to explain an oxygen exchange mechanism that returns the reactive intermediates to CaO.

Exxon (now ExxonMobil) reported that impregnation with 10-20% potassium carbonate lowers the optimum thermal gradients for steam gasification of bituminous coals, respectively, from 980 to 760°C and from 68 to 34 atm. The preferred form of make-up catalyst in their commercial-scale plant design was potassium hydroxide. This catalyst contributes to the overall process in a variety of ways. First, it accelerates gasification, allowing for a lower gasification temperature. Second, it reduces swelling and agglomeration when working with caking coals, which is another advantage of a lower gasifiers temperature. Most importantly, it encourages methanation because it is thermodynamically more favourable at lower temperatures. As a result, in this process, methane production is thermodynamically and kinetically favoured over synthesis gas. After the gasification stage, a catalyst retrieval unit is provided to recover the used catalyst.

CHAPTER 4

MOLTEN MEDIA GASIFICATION

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Molten media can refer to any of the foregoing: molten salt, molten metal, or molten slag. Molten media gasification occurs when salts of metallic elements and iron are used as a medium to carry out coal gasification. The molten medium not only catalyses the gasification reaction, but it also provides the required heat and acts as a heat exchange medium. 3,56 Over the years, some many distinct commercial processes have emerged:

1. The Kellogg-Pullman molten salt method

2. The molten iron gasification process at Atgas

3. Gasification of Rockwell molten salt

4. Gasification of Rummel-Otto molten salt

In this method, coal is gasified in a bath of molten sodium carbonate (Na2CO3) through which steam is passed. This process produces molten salt, which has the following advantages:

1. Because the steam-coal reaction is basic in nature, sodium carbonate strongly catalyses it, resulting in complete gasification at a low temperature.

2. Because molten salt disperses coal and steam throughout the reactor, direct gasification of caking coals without carbonization is possible.

3. A salt bath can be used to provide heat to the coal being gasified.

4. The product gas obtained is free of tars and tar acids due to the uniform temperature throughout the medium.

A stream of hot oven oxygen and steam picks up crushed coal from lock hoppers and transports it into the gasifier. Furthermore, sodium carbonate from the ash rejection system is metered into the transport gas stream, and the combined coal, salt, and carrier were also admitted to the gasifier. The majority of the preheated oxygen and steam is admitted into the reactor's bottom for passage through the salt bath in order to support the gasification reactions. Along with the usual gasification reactions, sulphur in the coal accumulates to an equilibrium level as sodium sulphide (Na2S). At this level, it exits the reactor via the following reaction:

$$Na_2CO_3 + H_2S \rightarrow Na_2S + CO_2 + H_2O$$

The ash accumulates in the melt and exits with the salt bleed stream, where it is rejected and sodium chloride is recycled. The salt bleed stream is quenched in water to dissolve sodium carbonate (Na2CO3) and allow filtration rejection of coal ash. The dilute solution of sodium carbonate is carbonated further to precipitate and recover sodium bicarbonate (NaHCO3). The filtrate is reused to cool the molten salt stream that exits the reactor. The sodium bicarbonate filtrate cake is dried and heated before being recycled to the gasifier as sodium carbonate. The gas stream that exits the gasifier is filtered to recover the entrained salt and heat before being converted to the desired product gas, such as synthesis gas, pipeline gas, or SNG (Figure 4.1).

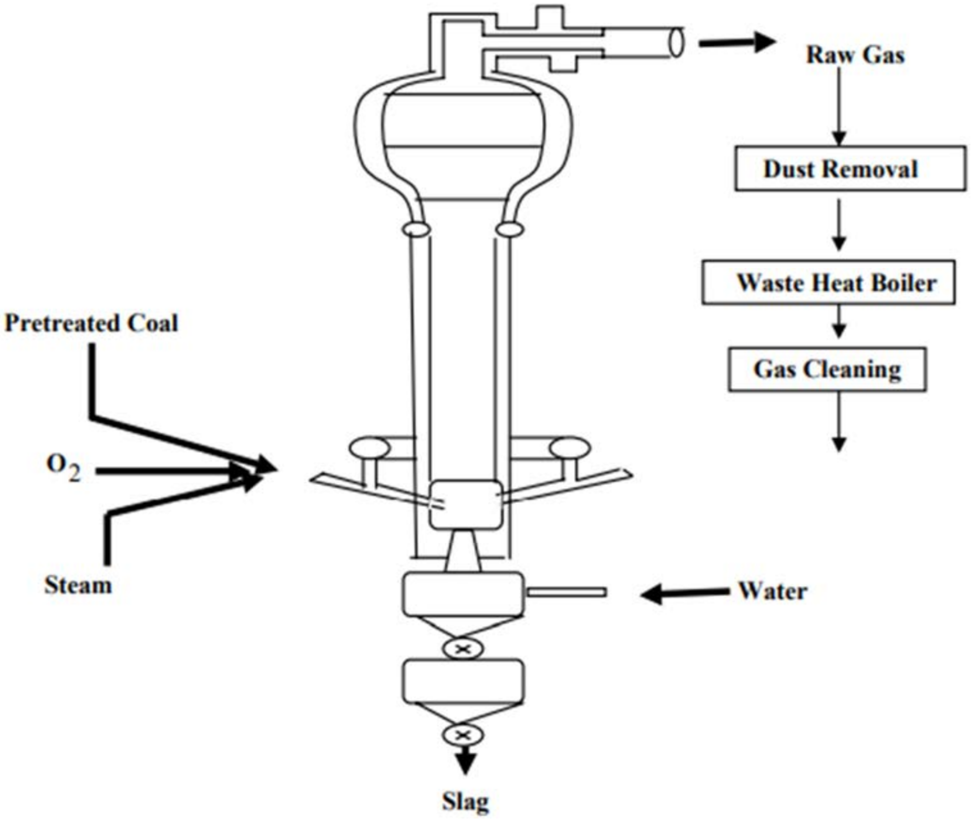

Figure 4.1 represent the Rummel-Otto single-shaft gasifier.

Atgas Molten Iron Coal Gasification

This method is based on the molten iron gasification concept, in which coal is injected into a molten iron bath with steam or air. Steam dissociation and thermal cracking of coal volatile matter produce hydrogen and carbon monoxide, which are the primary components of synthesis gas. The iron absorbs the coal sulphur and transfers it to a lime slag, from which elemental sulphur can be recovered as a byproduct. The dissolved coal in the iron is removed by oxidising it to carbon monoxide with oxygen or air injected near the molten iron surface. The Atgas process employs coal, steam, or oxygen to produce product gases with heating values of approximately 900 Btu/scf.

There are several inherent advantages to the Atgas molten iron process over gassolid contact gasification in either fixed or fluidized bed reactors.

58 They are as follows:

1. Because gasification occurs at low pressures, the mechanical difficulty of coal feeding in a pressurised zone is eliminated.

2. Coking properties, ash fusion temperatures, and coal fines generation are not problematic.

3. Coal's sulphur content has no environmental impact because it is retained in the system and recovered as elemental sulphur from the slag. The by-product elemental sulphur improves the overall process economics.

4. The system is highly adaptable to the physical and chemical properties of the feed coal. Particles of a relatively coarse size can be handled without any special pretreatment.

5. Tar formation is inhibited due to the extremely high temperature operation.

6. The product gas contains no sulphur compounds.

7. When compared to fixed bed or fluidized bed reactors, shutdown and startup procedures are greatly simplified.

Steam is used as a carrier gas to inject coal and limestone into the molten iron through tubes. Devolatilization occurs with some thermal decomposition of the volatile constituents, leaving the fixed carbon and sulphur to dissolve in iron, where carbon is oxidised to carbon monoxide. The sulphur migrates from the molten iron to the slag layer in both organic and pyritic forms (FeS2), where it reacts with lime to produce calcium sulphide (CaS). The product gas is cooled, compressed, and fed to a shift converter (WGS reactor) where a portion of carbon monoxide is reacted with steam via WGS reaction to achieve a CO-to-H_2 ratio of 1:3. The produced carbon dioxide is removed from the product gas, which is then cooled again. It is then passed through a methanator, where carbon monoxide and hydrogen react to produce methane via $CO + 3H_2 = CH_4 + H2O$. The excess water in the methanerich product is removed. The finished gaseous product has a heating value of approximately 900 Btu/scf.

Plasma Gasification

Plasma gasification is a nonincineration thermal process that decomposes input material into very simple molecules by using extremely high temperatures in an oxygen-free or oxygen-deprived environment. The extreme heat decomposes the input material into basic molecular structure species, aided by the absence of an oxidising agent such as oxygen. The plasma gasification or plasma pyrolysis process was initially developed for waste treatment. However, because of its high thermal efficiency, the process can be very effectively applied to coal gasification or oil shale pyrolysis, as long as the input energy for plasma generation can be obtained effectively via energy integration or some other inexpensive source of energy. When plasma gasification is used on carbonaceous materials like coal and oil shale kerogen, the byproducts are typically a combustible gas and an inert slag. Traditional technologies such as cyclones, scrubbers, and ESPs can be used to clean product gas. Normally, cyclone/scrubber effluent can be recycled for further processing.

The fourth state is frequently mentioned as plasma. Electricity is fed into a plasma torch with two electrodes, which creates an arc through which inert gas flows. The inert gas heats the process gas to extremely high temperatures, up to 25,000°F. A few feet away from the torch, the temperature can reach 5,000-8,000°F, at which point the carbonaceous materials are completely destroyed and broken down into their elemental forms. In addition, no tar or furan is used or produced in just this process. The ash or mineral matter would become completely molten and flow out of the reactor's bottom. As a result, the plasma reactor is not limited to a single type of coal for gasificatiodepicts how the blood torch works.

Plasma gasification has unique advantages for the protection of air, soil, and water resources when applied to waste materials such as municipal solid waste (MSW) due to extremely low limits of air emissions and leachate toxicity. Because the process does not rely on the combustion of carbonaceous materials, it produces far fewer greenhouse chemicals, particularly carbon dioxide, than any other conventional gasification technology. In addition, air emissions are typically orders of magnitude lower than the current regulations. The slag is solid, and the leachate is liquid (Figure 4.2).

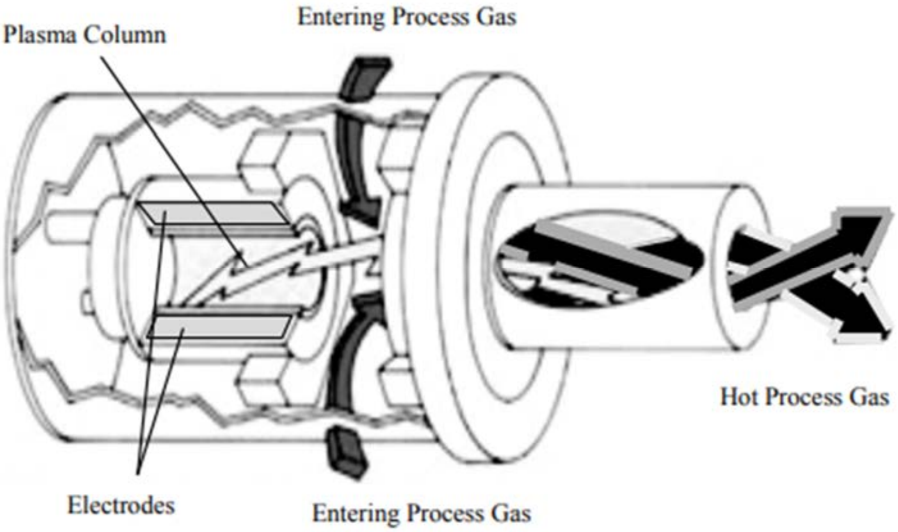

Figure 4.2 represent the Plasma torch.

Levels are orders of magnitude lower than the current EP-toxicity standard, which is one of four criteria used to classify hazardous waste. Slag weight and volume reduction ratios are typically very high; for example, biomedical wastes have ratios of 9:1 and 400:1, respectively. Despite the fact that data for a variety of coals is not readily available in the literature, both the mass reduction ratio and the volume reduction ratio for coals are thought to be significantly higher than those for nonplasma gasification technology, thereby significantly reducing the burden of waste and spent ash disposal.

Activities in Canada and Norway are noteworthy in the development of plasma gasification technology. Resorption Canada Limited (RCL) is a private Canadian company that was federally incorporated to develop and market plasma arc-based industrial processes. They have extensive operational experience in this technology, with input materials ranging from environmental to biomedical to energy-related materials and resources.

Mathematical Modeling Of Coal Gasifiers

As new and efficient coal gasification concepts are developed, mathematical modelling provides insight into their operation and commercial potential. Before any commercial processes are designed, the impact of design variables and processing conditions on gasifier performance must be determined a priori. These models are then used as design tools for modification, scaling, and optimization.

Coal gasification takes place in various types of reactors, with the bed moving, fluidized, entrained, or made up of molten salts depending on the type of gas-solid contact. Because of its high coal conversion rates and thermal efficiency, a moving bed configuration may be the most widely used of these. To model various types of reactors, various approaches have been used. There are primarily two types of models. The first type is the thermodynamic or equilibrium model, which is simpler to develop but produces only limited information, such as offgas compositions in a limiting case. The kinetic model, on the other hand, predicts kinetic behaviour inside the reactor. The process's time-dependent behaviour can be either steady state or dynamic. Adanez and Labiano created a mathematical model of an atmospheric moving bed countercurrent coal gasifier and investigated how different operating conditions affect gas yield and composition, process efficiency, and longitudinal temperature profiles. For adiabatic reactors, the model was created. It is assumed that the gasifier is divided into four zones, each with its own set of physical and chemical processes.

They are the zones for coal preheating and drying, pyrolysis, gasification, and combustion, followed by the ash layer, which acts as a preheater of the reacting (i.e., entering) gases. In reality, there is no physical distinction between the zones, and the reactions that occur in each zone vary significantly. To define the reaction rate of the coal particles, the model employs the unreacted shrinking core model. The unreacted shrinking core model assumes that as the coal is reacted, the dimension (often represented by particle size) of the unreacted core (of the remaining coal particle) shrinks progressively.

The longitudinal temperature profile is the most critical parameter in the operation of these moving bed gasifiers with dry ash extraction, because the temperature inside the reactor must not exceed the ash-softening (or ash-oozing) point at any time to avoid ash fusion or oozing. The model also considers the effects of coal reactivity, particle size, and the steam/oxygen ratio. To test the model's validity, predicted data based on the model were compared to real data on the product gas composition of various coals, and good agreement was obtained. The authors concluded that the reactivity of the coals and the emissivity of the ash layer must be accurately known because they have a strong influence on the temperature profiles, the maximum temperature in the reactor, and its capacity for coal processing.

Lim et al. created a mathematical model of a spouted bed gasifier based on first-order reaction kinetics for gasification reactions. The spouted bed gasifier is currently being developed in Canada and Japan. The spout is modelled as a fixed-diameter plug flow reactor (PFR) with cross-flow into the annulus. The annulus is thought of as a series of steam tubes, each of which is a plug flow reactor with no axial dispersion. The model computes the composition profiles of various product gases in the spout as a function of height, radial composition profiles and average compositions in the annulus at various heights, average compositions exiting the spout and annulus, and flow rates and linear velocities in the spout and annulus. The model was expanded into a two-region model with an enthalpy balance.

A similar model for simulating the performance of a cross-flow coal gasifier has been developed by Monazam et al. The process of gasification in a cross-flow gasifier is similar to batch gasification in a combustion pot. As a result, the model equations for kinetics, as well as mass and energy balances, were developed in a batch process. Operating temperatures in the cross-flow coal gasifier concept are much higher than 1000°C, so diffusion through the gas film and ash layer is critical. For kinetic formulations, the model also assumes a shrinking unreacted core model. The model's simulation results were compared to experimental data from batch and countercurrent gasification experiments, and good agreement was obtained. It was also determined that the gasifier's performance is determined by the gas-solid heat transfer coefficient, whereas particle size and bed voidage have a significant effect on the time required for complete gasification.

Watkinson et al. created a mathematical model to predict the composition and yield of gas from coal gasifiers. The composition of the gas is determined by the contacting pattern of the blast and fuel, the temperature and pressure of the operation, the composition of the blast, and the method of fuel feeding. The authors presented a calculation method and compared the predicted data to operating data from nine different types of commercial and pilot-scale gasifiers, including Texaco, Koppers-Totzek, and Shell, Winkler-fluidized bed, and Lurgi dry ash, and Lurgi slagging moving bed gasifiers. The model includes elemental mass balances for carbon, hydrogen, oxygen, nitrogen, and sulphur, chemical equilibria for four key chemical reactions, and an optional energy balance. Partial oxidation, steam gasification, the Boudouard reaction, and the WGS reaction were the four key reactions. Predictions for entrained flow systems were most accurate, less accurate for fluidized bed gasifiers, and uncertain for moving bed reactors. This was due to lower temperatures and uncertain volatile yields in the latter, which resulted in a difference between calculated and experimentally reported values.

Lee et al. created a single-particle model to interpret coal char gasification kinetic data with H2, CO_2, and H_2O. Their model generates asymptotic analytical solutions by accounting for all of the major physical factors that influence and contribute to the overall gasification rate. Changes in the magnitudes of internal surface area, porosity, activation energy, and effective diffusivity as a function of conversion were among the factors considered (or burnoff). Their model accurately depicts the shape of the conversion vs. time curves determined by CO_2 gasification studies.

Under certain constraints, the curve shape leads to a "universal curve" of conversion vs. an appropriate dimensionless time. The developed model is very simple mathematically, and all of the parameters in the model equation have physical significance. As a result, the model is applicable to a wide range of coals with varying physicochemical and petrological properties. In this model, there are only two adjustable parameters. Their model predictions were compared to experimental data obtained using a novel thermobalance reactor, and they achieved excellent agreement. In their review, Gururajan et al. critically examined many of the mathematical models developed for fluidized bed reactors. The review focuses on the modelling of bubbling fluidized bed coal gasifiers. They also discuss the rate processes that occur in a fluidized bed reactor and compare their presentation to some of the reported models in the literature.

When coal is fed into a gasifier, it goes through several physicochemical transformations, including (1) drying, (2) devolatilization, and (3) gasification of residual char in various gaseous atmospheres. These heterogeneous reactiontransport phenomena are accompanied by a number of homogeneous supplementary reactions. In order to develop a mathematical model, detailed kinetic studies are required. There are two types of mathematical models for a bubbling fluidized bed coal gasifier: thermodynamic (or equilibrium) models and kinetic (or rate) models. Based on a given set of steam/oxygen feed ratios, operating pressure, and desired carbon conversion, thermodynamic models predict the equilibrium compositions and temperature of the product gas.

These models are independent of gasifier type and are based on the assumption of total oxygen consumption. As a result, they cannot be used to study the effect of operating parameters on gasifier performance. The kinetic model, on the other hand, predicts the composition and temperature profiles inside the gasifier for a given set of operating conditions and reactor configurations and can thus be used to assess the gasifier's performance. They are created by combining an appropriate hydrodynamic model for the fluidized bed with kinetic schemes for the reactive processes that occur inside the gasifier. Based on the hydrodynamic models used, various rate models can be classified into four groups. They are as follows:

1. Flow models that have been simplified
1. Models of the Davidson-Harrison type
2. Models of the Kunii-Levenspiel type
3. Models of the Kato-Wen type

The same review investigated and compared various types of models.

Despite the fact that many researchers have compared their model predictions to experimental data, no detailed evaluation of the influence of model assumptions on model predictions has been reported. Although efforts have been made to compare the predictions of different models, no attempt has been made to evaluate the model using experimental data from various sources. In their review article, Gururajan et al. developed their own model for a bottom feeding bubbling fluidized bed coal gasifier based on the following assumptions:

1. The bubble phase is in plug flow and has no particles, whereas the emulsion phase is completely mixed and has particles in fluidized conditions.

2. Excess gas from the emulsion phase enters the bubble phase.

This excess per unit bed volume occurs at a constant rate.

3. The feed coal particles are spherical, homogeneous, and uniform in size.

4. Only the WGS reaction takes place in the homogeneous gas phase.

5. In the char gasification reactions, external mass transfer and intraparticle diffusion are assumed to be negligible.

6. Bed particle entrainment, abrasion, agglomeration, or fragmentation are assumed to be negligible.

7. The gasifier is in an isothermal steady state.

All of the model equations are derived from the preceding assumptions.

The predictions of the model were compared to experimental data from three pilotscale gasifiers reported in the literature. They concluded that the predictions were more sensitive to assumptions about volatile combustion/decomposition and char combustion products than to the rate of char gasification. As a result of the short residence time of coal particles in pilot-scale gasifiers, carbon conversion and product gas yields are primarily determined by fast-rate coal devolatilization, volatiles combustion/decomposition, and char combustion, as well as slow-rate char gasification reactions. This explains how models based on finite-rate char gasification reactions can fit the same pilot-scale data.

A better understanding of coal devolatilization, volatile decomposition, and char combustion in a fluidized bed coal gasifier is critical for the development of a model with good predictive capability. There is a strong need to investigate the kinetics of coal and char gasification in synthesis gas atmospheres, as well as to collect experimental data for the same coal and char in a pilot-scale plant. It is well understood that many physical changes occur when coal char particles are gasified. Many attempts have been made to normalise these dynamic changes using various normalising parameters such as half-life, coal rank, reactivity, or surface area. According to Raghunathan and Yang, experimental char conversion vs. time data from various experiments can be unified into a single curve where time is considered to be normalised time, t/t1/2, t1/2 being the char-gas reaction's half-life. This unification curve with only one parameter is then fitted into commonly used rate models, such as the grain model and the random pore model. A master curve is derived using reported correlations for unification curves to approximate the conversion-time data for the majority of gasification systems. Furthermore, because the half-life (or, more precisely, the half-conversion time) is simply related to average reactivity, it can be used as a reactivity index to characterise various char-gas reactions. Furthermore, conversions of up to 70% can be predicted with reasonable accuracy across a wide temperature range.

A significant amount of effort has gone into mathematically modelling a variety of gasifiers and reaction conditions in order to obtain design and performance information. Numerous simplified models and asymptotic solutions for coal gasification reactors have been obtained, as well as a large database of digital simulation of such systems.

CHAPTER 5

CLEAN LIQUID FUELS FROM COAL

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Pyrolysis of coal produces condensable tar, oil, water vapour, and noncondensable gases via a process known as destructive distillation, which involves cleavages of C-C bonds in the coal macromolecular structure. The C-C bond cleavage reactions are largely responsible for the reduction in molecular weight in coal hydrocarbons, which eventually converts solid fuel to liquid or gas. Char is the solid residue of coal pyrolysis that is left behind. As a result, char contains significantly less volatile hydrocarbons than coal and has a lower H content. The H/C ratio, as implied, is an effective indicator of the nature of coal product. For example, the formation of coal char from coal decreases as the H/C ratio decreases, whereas coal liquid conversion increases as the H/C ratio decreases. To remove sulphur and nitrogen species and improve liquid fuel quality, the condensed pyrolysis product must be hydrogenated further. When nitrogen and sulphur species are combusted, they not only produce air pollutants (NOx and SOx) but also poison and deactivate the upgrading catalyst. Pyrolysis, as the name implies, involves thermal decomposition reactions that primarily cause the cleavage of C-C bonds and the partial breakdown of C-S and C-H bonds within the macromolecular structure of coal, resulting in lower molecular weight products such as liquid hydrocarbons.

There are several commercially available coal pyrolysis processes. shows the various coal pyrolysis processes, as well as their operating conditions and yields. The coal rank, coal particle size, reactor type, process mechanics, hydrogen partial pressure, reactor pressure, processing temperature, coal residence time, and other factors all have an impact on process efficiency and product yield. suggests that shorter residence times result in higher liquid yields, and that the hydrogen atmosphere aids the liquid product yield. If properly managed, a shorter residence time does not allow for enough reaction time to thermally crack the liquid hydrocarbons further (to gaseous hydrocarbons), leaving more liquid hydrocarbons in the product stream. Adding hydrogen to coal hydrocarbons raises the H/C ratio to a level sufficient to produce a liquid fuel. The high tar content in supercritically retrieved coal products could be attributed to the supercritical solvent's excellent low-temperature solubility, which extracts and dissolves the tar in its entirety. The extraction of large molecular weight hydrocarbons in this low-temperature operation is primarily due to the superior solvent properties of supercritical fluids, rather than the C-C bond breakage reaction of coal pyrolysis.

Coed Process

The FMC Corporation pioneered the COED (Char-Oil-Energy-Development) process. The process has been enhanced, and the enhanced version is now known as the COED/COGAS process. The process is based on fluidized bed technology and is performed in four successive fluid bed pyrolysis stages at increasing temperatures. The optimal temperatures for the four stages differ depending on the feed coal's properties. The temperatures of the stages are chosen to be just below the maximum temperature that the specific feed coal can be heated to without agglomerating and plugging the fluid bed. In the first, second, third, and fourth stages, typical operating temperatures are 315-345°C, 425-455°C, 540°C, and 870°C, respectively. In the fourth stage, a portion of the product char is burned with a steam-oxygen mixture to provide heat for the process. Hot gases flow countercurrently to the char, creating a hot fluidizing medium for the pyrolysis stages. The gases from the first and second stages are routed to cyclones, which remove the fines; however, the vapours from the cyclones are quenched in a Venturi scrubber to condense the oil, and the gases and oil are separated in a decanter. Desulfurization of the gas is followed by steam reforming to produce hydrogen and fuel gas. The oil poured from the decanter. In a shift kiln, the char is treated with hydrogen to produce hydrogen sulphide (H_2S), which is then absorbed by an acceptor such as dolomite or limestone. The COGAS process involves gasifying COED char to create a gas mixture ($CO + H_2$). This COED/COGAS process is significant in terms of both liquefaction and gasification.

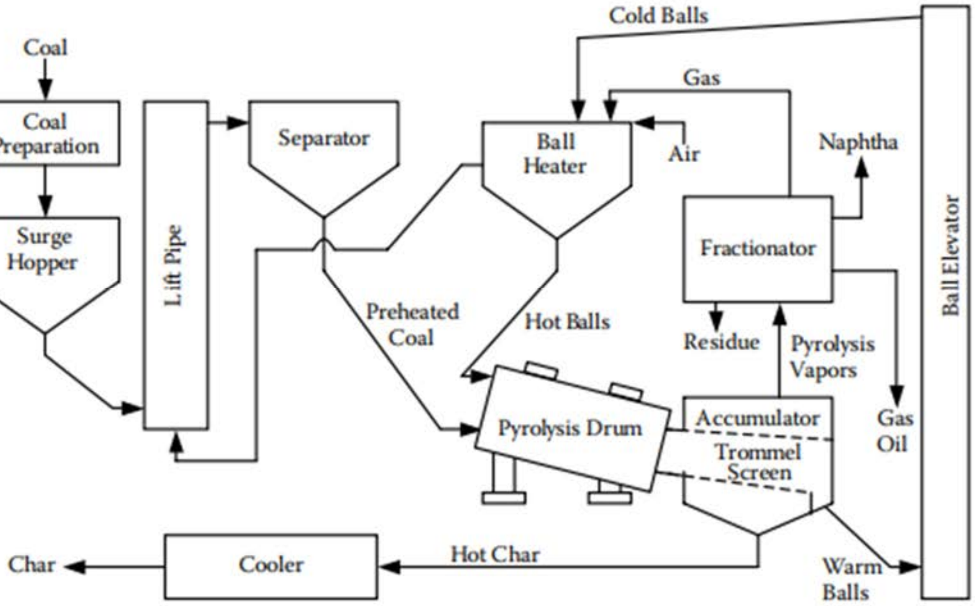

Figure 5.1 represent the TOSCOAL process.

The residual char is drawn off and separated from the ceramic balls in a revolving drum with holes in it. In a separate furnace, the ceramic balls are reheated by burning some of the product gas. TOSCOAL is similar to the TOSCO process for producing overhead oil from oil shale. In this process analogy, char is used to replace spent shale, while raw coal is used to replace raw oil shale. 1,38 It should be noted that TOSCO is an abbreviation for the Oil Shale Corporation.

The properties of liquids produced by the TOSCOAL process from Wyodak coal). The recovery efficiency is nearly 100%, as demonstrated. It should be noted that the recovery efficiency is calculated using the total material balance concept, rather than the conversion efficiency towards coal liquid or coal gas. As a result, the high water recovery rate is due to the nature of the feed coal. Wyodak coal is coal from the Tongue River Member of the Fort Union Formation in Wyoming's Powder River Basin. It has a subbituminous rank and a heating value of 8,200-8,300

Btu/lb. It has an average ash content of 5-6% and less than 0.5% sulphur. It is no coincidence that the TOSCOAL process has a similar processing temperature to the TOSCO oil shale process.

Lurgi–Ruhrgas Process

The Lurgi-Ruhrgas (L-R) process was created as a low-pressure method of producing liquid from lower rank coals. This European-developed process is now in commercial use. Figure 5.2 depicts a flowchart of this process. Crushed coal is fed into a mixer and quickly heated to 450-600°C by direct contact with hot recirculating char particles that have previously been heated in a partial oxidation process in an entrained-flow reactor. A cyclone separates the fines from the product gases, and a series of condensers collect the liquid products. The liquid products are hydrotreated to produce higher-quality products. The relatively long residence time accounts for the high gas yield, and the gaseous products include both primary and secondary products. The term secondary product is used to emphasise that the product is not created directly from coal.

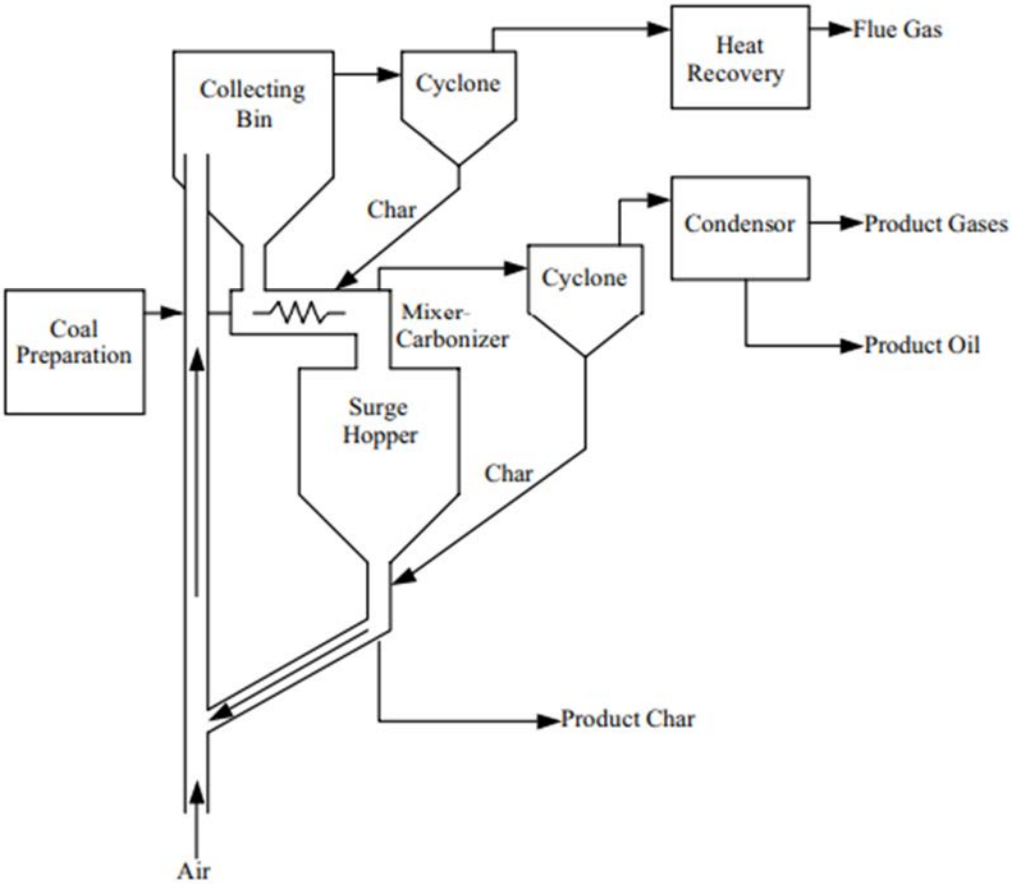

Figure 5.2 Lurgi-Ruhrgas Process.

Occidental Flash Pyrolysis Process

Hot recycle char is used in this process to provide heat for the flash pyrolysis of pulverised coal in an entrained flow reactor at temperatures not exceeding 760°C. The process has a short residence time, which increases coal throughput and increases the production of liquid eyeliners while decreasing the production of gaseous products. Pyrolytic decomposition of fuel hydrocarbons into liquid-range hydrocarbons occurs actively during a short residence time at a high temperature, but their further conversion into gaseous hydrocarbons is less noticeable. Before quenching in the two-stage collector system, cyclones, like other processes, remove fine char particles from the pyrolysis overhead. 1 The first stage involves quenching at approximately 99°◦ c. the majority of heavier hydrocarbons, followed by quenching at approximately 25°C to remove water and light oils (i.e., lower molecular weight hydrocarbons).

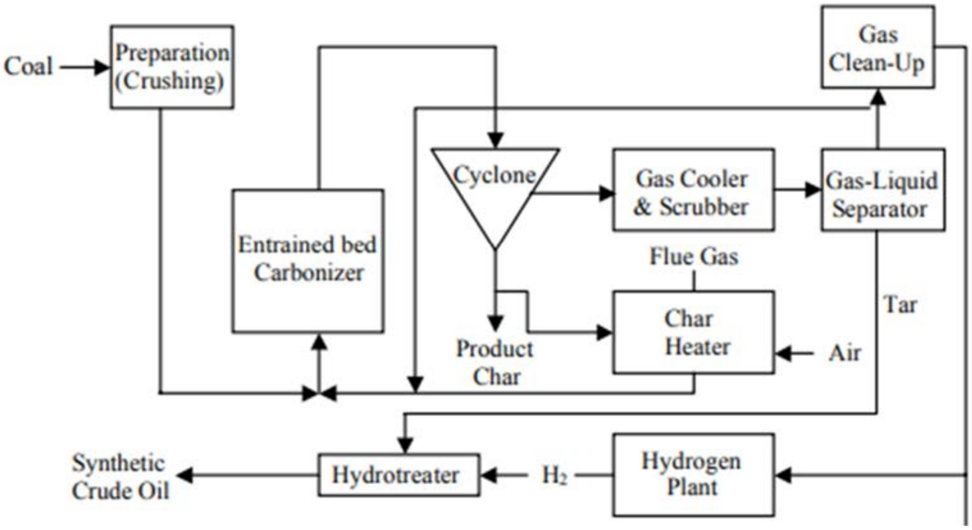

Figure 5.3 Represent the flash pyrolysis process.

Clean Coke Process

The method involves feeding oxidised clean coal into a fluidized bed reactor at temperatures as high as 800°C, where the coal reacts to produce tar, gas, and low-sulfur char. Alternatively, noncatalytic hydrogenation at 455-480°C and pressures of up to 340 bar of hydrogen can be used to process the coal. The process of direct hydrogenation of coal involves the addition of hydrogen to the coal hydrocarbons while cracking the high-molecularweight liquid fuels into lower molecular weight hydrocarbons, raising the H/C ratio of the fuel to that of liquid hydrocarbon fuel. The liquid products of the carbonization and hydroxylation stages are combined and processed further to produce synthetic liquid fuels.

Coalcon Process

This method employs a noncatalytic fluidized bed of diesel fuel particles suspended in hydrogen gas. Hot, oxygen-free flue gas is used to heat the coal to around 325°C and to transport it to a feed hopper. The overhead stream is divided into four streams using a fractionator: (1) gases (H_2, CO, CO_2, and CH_4), (2) light oil, (3) heavy oil, and (4) water. The majority of the char has been removed from the reactor's bottom, quenched with water, and cooled. 1 The char can then be fed into a Koppers-Totzek gasifier, where it will react to oxygen and steam to produce hydrogen for the process.

This means that the liquefaction process has been carried out in a hydrogen environment. Direct liquefaction can be divided into one or two stages. In two-stage processes, the coal is first hydrogenated in a liquid-phase stage, transforming it into a deashed, liquid product, and then catalytically converted to clean, light distillate fuels in a second vapor-phase stage. Direct liquefaction has a relatively long history, and various large-scale processes have been successfully implemented. Large-scale coal liquefaction operations, in turn, contributed significantly to the advancements of chemical process industries in all aspects of machinery, design, and knowledge. H-Coal, SRC-I, SRC-II, EDS, ITSL, CC-ITSL, and CTSL 6are recent processes that are ready for demonstration or full commercialization.

bergius-ig hydroliquefaction process

The Bergius process, which was a two-stage process, was used very successfully in Germany before and during World War II. It is no longer in use, but it has made significant contributions to the advancement of catalysed coal liquefaction technology. At 450-500°C and 200-690 bars (197-681 atm, or 20-69 MPa), coal (slurried with heavy oil) is catalytically converted in the presence of hydrogen and an iron oxide catalyst. Light oils, middle distillates, and residuum were typically separated from the products. Middle distillates, also known as mid-distillates, are refined petroleum products that include heating oil, distillate fuel oil, jet aviation fuel, and kerosene. In general, the boiling range of mid-distillates is 300-750°F, and that of residuum is 600-1000°F.

Except for residuum, these oils were catalytically cracked to motor fuels and light hydrocarbons in a vapor-phase hydrogenation stage, which serves as the process's second stage. Some argue that the harsh conditions used in the original process were necessary because German coals are far more difficult to liquefy than coals from the United States. From a technological standpoint, it is truly remarkable that the process was successfully operated on the a large scale in the 1940s, despite the harsh process conditions of a hydrogen atmosphere. The catalytic conversion residence time was approximately 80-85 minutes, which was quite long, and hydrogen consumption was quite significant approximately 11% by mass of the daf (dry ash-free) coal.

h-coal process

Hydrocarbon Research, Inc. (HRI), now Hydrocarbon Technologies Inc., developed the H-Coal process for direct catalytic diesel fuel liquefaction in 19. (HTI). The process was developed in stages, beginning with conceptualization and progressing to bench-scale (25 lb/d), process development unit (PDU) (3 tons/d), and a pilot plant in Catlettsburg, KY (200-600 tons/d). The US Department of Energy (DOE), the Commonwealth of Pennsylvania, EPRI, Mobil, AMOCO, CONOCO, Ruhrkohle, Ashland Oil, SUN Oil, Shell, and ARCO all contributed $300 million to this pilot plant project (Figure 5.4).

The ebullated-bed reactor combines pulverised coal, recycle liquids, hydrogen, and a catalyst to convert coal into hydrocarbon liquids and gaseous products. The catalyst pellets are 0.8 to 1.5 mm diameter extrudates, and the pulverised coal has a mesh size of -60. The term -60 mesh refers to the particle fraction that passes through the 60-mesh screen, i.e., the particle size in this fraction is smaller than the 60-mesh screen's hole opening. Coal slurried with recycle oil is pumped to up to 200 bar pressure and introduced into the bottom of the ebullated-bed reactor. The development of the H-Coal process has made significant contributions to the field of chemical reaction engineering, particularly in the areas of multiple phase reactions and the design of ebullated and liquid-entrained reactors. A gas-liquid-solid fluidized bed reactor is similar to a liquid entrained reactor, but much larger gas bubbles help fluidize the solid particles. As a result, large coal particles can be used in the ebullated bed reactor.

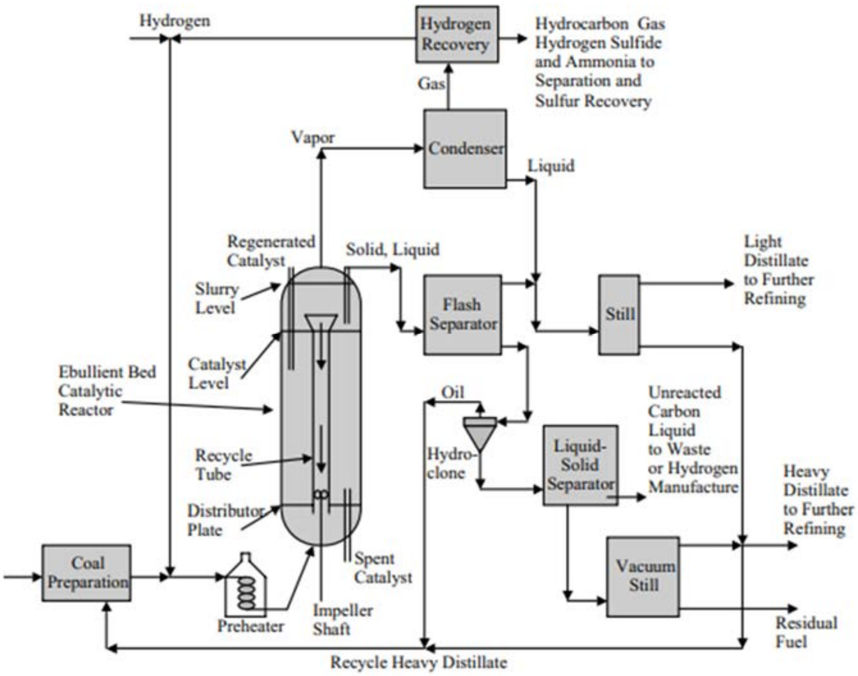

Figure 5.4 H-coal process.

Solvent Refined Coal (Src-I)

In 1962, Spencer Chemical Co. began developing a process that was later adopted by Gulf Oil Co., which designed a 50-ton/d SRC production plant at Fort Lewis, WA in 1967 From 1974 to late 1976, the plant was run in SRC-I mode. Southern Services Co. (SSC) and General Electric Institute (EEI) designed and built a 6-ton/d SRC-I pilot plant in Wilsonville, AL, in 1972 (Figure 5.5).

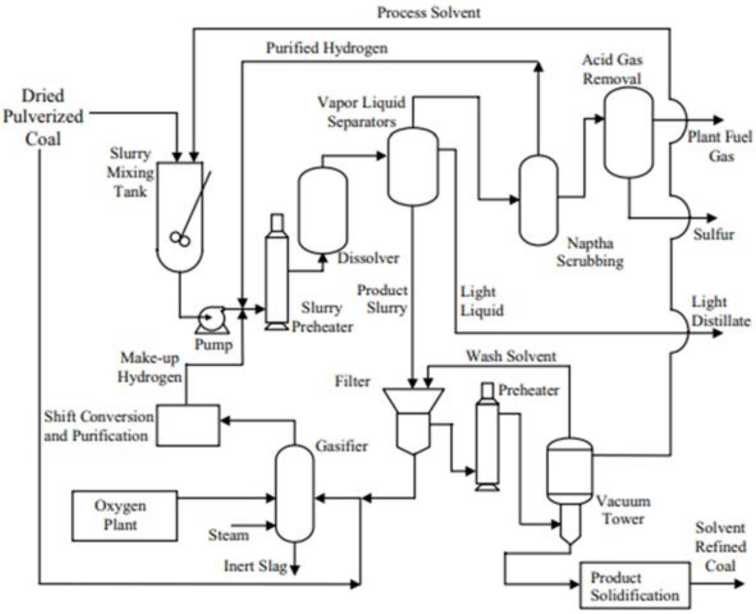

Figure 5.5 SRC-I process.

The original SRC-I process's main goal was to create a solid boiler fuel with a melting point of around 150°C and a thermal efficiency of 16,000 Btu/lb. In order to improve commercial potential, the product line was expanded to include liquids produced by a Coker/Calciner and an Expanded-Bed Hydrocracker. SRC-I is a thermal liquefaction operation in which a solvent, coal, and hydrogen react in a "dissolver" reactor to produce a nondistillable residue that can be used as a clean boiler fuel after deashing. The reaction conditions are milder than in the H-Coal process. The lack of a catalyst reduces hydrogenation rates, and the residue has a H/C ratio similar to the coal feed. Again, this process is ideal for bituminous coals, particularly those with high pyrite concentrations. Pyrite is thought to be the liquefaction catalyst. A diagram of the SRC-I process

The benefits and drawbacks of SRC-I are listed.

1. Vacuum distillation cannot be used to remove nondistillable SRC-I residues.
2. Extraction-type separation methods were specifically designed for this process.

Kerr-Critical McGee's Solvent Deashing is an example of this (CSD). A light aromatic solvent is used in this deashing process to precipitate the heaviest (toluene-insoluble) fraction of the residue, as well as all of the ash and unconverted coal. This method recovers a solid-free but heavy recycle solvent.

Exxon Donor Solvent (Eds) Process

The EDS process liquefies coal using a noncatalytic hydroprocessing step to produce liquid hydrocarbons. The hydrogenation of the recycle solvent, which is used as a hydrogen donor to the slurried coal in a high-pressure reactor, is its distinguishing feature. This is also considered a single-stage process because both coal dissolution and residence upgrading occur in the same thermal reactor. The liquefaction reaction occurs without the use of a catalyst. However, the recycle solvent is catalytically hydrolyzed in a separate fixed-bed reactor. This solvent is in charge of transferring hydrogen from the high-pressure liquid to the slurried coal (Figure 5.6).

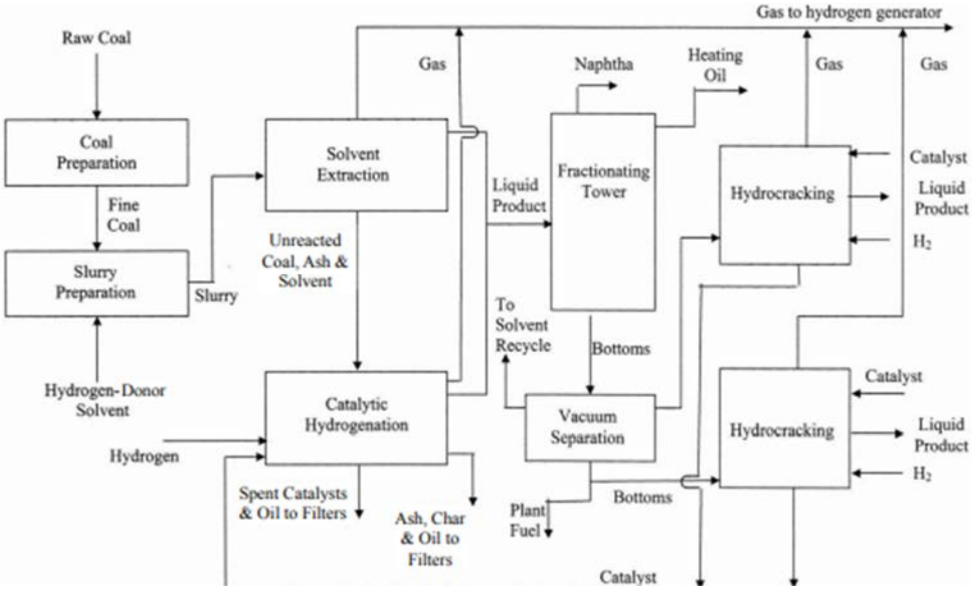

Figure 5.6 Exxon Donor Solvent.

To be an effective hydrogen donor, EDS solvent must be well hydrogenated. The recycle solvent "donates" hydrogen to the primary liquefaction products, resulting in rapid hydrogenation. This is followed by thermal hydrogenation and cracking to produce distillates. Due to the lack of a hydrotreating catalyst, the product quality is slightly lower than that of H-Coal. Distillate harvests are also lower when compared to the H-Coal process. Because of the less expensive thermal reactor and the simple solids removal process, its overall process economics are comparable to the H-Coal process. The EDS process began with bench-scale research in the mid-1960s and progressed to a pilot plant study on a 1 ton/d scale in the 1970s and 1980s. The initial process development programme was entirely under Exxon's control, whereas the later part of development has been cosponsored as a joint venture between Exxon and the US DOE. The Exxon Coal Liquefaction Plant (ECLP) was built and put into operation in 1980 as a large-scale (250 tons/d) demonstration type of installation. The plant was decommissioned and demolished in 1982.

SRC-II PROCESS

Instead of the solid products produced by SRC-I, the SRC-II process uses direct hydrogenation of coal in a reactor at high pressure and temperature to produce liquid hydrocarbon products. The 50-ton-per-day pilot plant at Fort Lewis, Washington, which ran in the SRC-I mode from 1974 to 1976, was converted to the SRC-II mode, producing liquid products for testing. From 1978 to 1981, the pilot plant was successfully operational. The SRC-II process is a thermoelectric process that relies solely on the mineral matter in coal as a catalyst. The recycle of the heavy oil slurry keeps the mineral matter concentration in the reactor high. The use of recycled mineral matter and the more severe reaction conditions distinguish the SRC-II process from the SRC-I process, as do the lighter products. The net product is a -540°C distillate recovered through vacuum distillation. The term -540°C distillate refers to the fraction of the distillation temperature that falls below 540°C. The vacuum bottoms, which include ash, are gasified to generate process hydrogen. Because the SRC-II process is limited to coals containing catalytic mineral matter, it excludes all lower-rank coals and some bituminous coals. SRC-II employs pulverised coal with particle sizes smaller than 0.125 in. and a solvent-to-coal ratio of 2.0, whereas SRC-I employs a solvent-to-coal ratio of 1.5.

Nonintegrated Two-Stage Liquefaction (Ntsl)

Despite the fact that single-stage processes such as EDS, SRC-I, SRC-II, and H-coal are technically sound, their process economic growth suffer for the following reasons:

1. The severity of the reaction is high, with temperatures ranging from 430 to 460°C andliquid residence times ranging from 20 to 60 minutes. These harsh operating conditions were deemed necessary in order to achieve coal conversion rates of more than 90% (to tetrahydrofuran (THF) or quinoline solubles).

2. Distillate yields are low, with mmaf (mineral matter and ash free) bituminous coals yielding only about 50% and subbituminous coals yielding even less.

3. Hydrogen efficiency is low due to high hydrocarbon gas yields.

4. The costs associated with the SRC-I process or something similar may be prohibitively expensive for producing boiler fuel.

Because of these considerations, a coal lng process is best suited for producing higher-value-added products such as transportation fuels. The resid must first be hydrocracked to distil liquids in order to produce higher value-added products from the SRC-I process. Mobil and Chevron's efforts on fixed-bed hydrocracking were not entirely successful due to ash plugging and rapid deactivation of the catalyst by coking.

LC-Fining (Lummus-Cities-Fining), a variation of ebullated-bed technology developed by Cities Services R&D, successfully hydrotreated the SRC-I residence. As a result, a hydrocracking component was added to the SRC-I process, resulting in Nonintegrated Two-Stage Liquefaction (NTSL). This unusual name was chosen because the hydrocracking component did not provide solvent to the SRC-I component. In other words, the NTSL process was a hybrid of two distinct processes: coal liquefaction and residential upgrading (Figure 5.7).

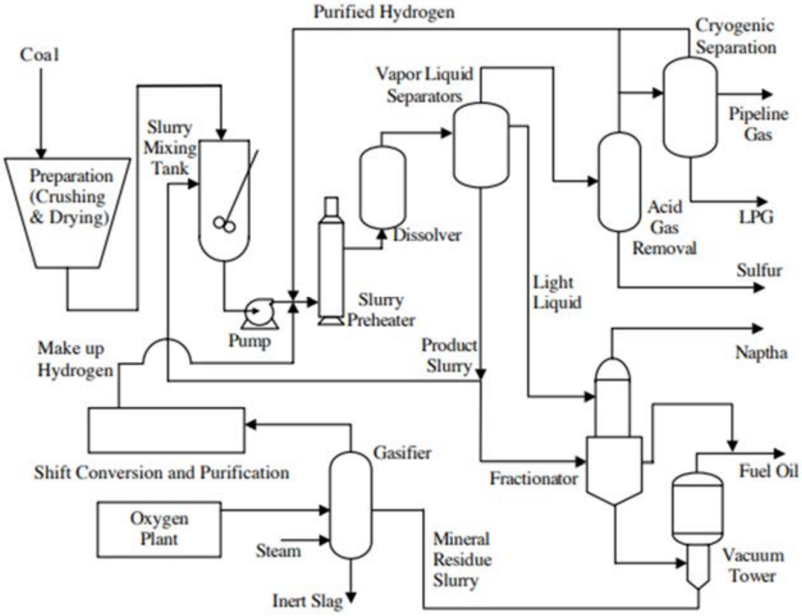

Figure 5.7 SRC-II process.

because of the shortcomings mentioned earlier. Because SRC-I is a less reactive feed to hydrocracking, it necessitates high temperatures (above 430°C) and low space velocity (i.e., low productivity) for complete conversion to distillates. Resid conversion was kept below 80% to keep the temperature and reactor size within reasonable limits. Although yields were higher than for H-coal, hydrogen consumption remained high due to the extensive thermal hydrogenation step in the SRC-I dissolver, which was renamed the Thermal Liquefaction Unit (TLU).4 NTSL had a brief existence, and a newer integrated approach was later developed.

Thermal Integrated Two-Stage Liquefaction

Thermal coal dissolution studies conducted by Consol, Mobil, and Wilsonville in the late 1970s revealed that coal conversion to tetrahydrofuran-solubles is essentially complete in 1-5 minutes. During this brief dissolution period, hydrogenation from the gas phase is negligible, and almost all hydrogen in the liquid phase comes from the solvent. If the amount of hydrogen relocated from the solvent is insufficient to meet the liquefaction requirements, the product will have a high concentration of tolueneinsolubles, causing precipitation and plugging in the reactor or downstream equipment. Short contact time (SCT) liquefaction is the preferred thermal dissolution procedure with a well-hydrogenated solvent, however, because it eliminates the inefficient thermal hydrogenation inherent in the SRC-I. Cities Services R&D successfully hydrocracked the SRC-I resids by LC-Fining at relatively low temperatures of 400-420°C. The yield of gas was low, but the efficiency of hydrogen was high. Combining this process with SCT is unquestionably a good idea, and it serves as a successful example of process integration. The minimal LC-Fining provides the liquefaction solvent to the first stage SCT, resulting in the integration of the two stages. This combination has the potential to liquefy coal and distillate products more efficiently than any single stage process.

CHAPTER 6

LUMMUS ITSL

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Lummus created an ITSL process that combined SCT and LC-Fining. Figure 6.1 depicts a process chart of the Lummus ITSL process. In the SCT reactor, coal is slurried with recycled solvent from LC-Fining and converted to quinoline-solubles (or THF-solubles). In the LC-Fining stage, the residue is hydrocracked to distillates, and recycle solvent is produced. The ash is extracted by the

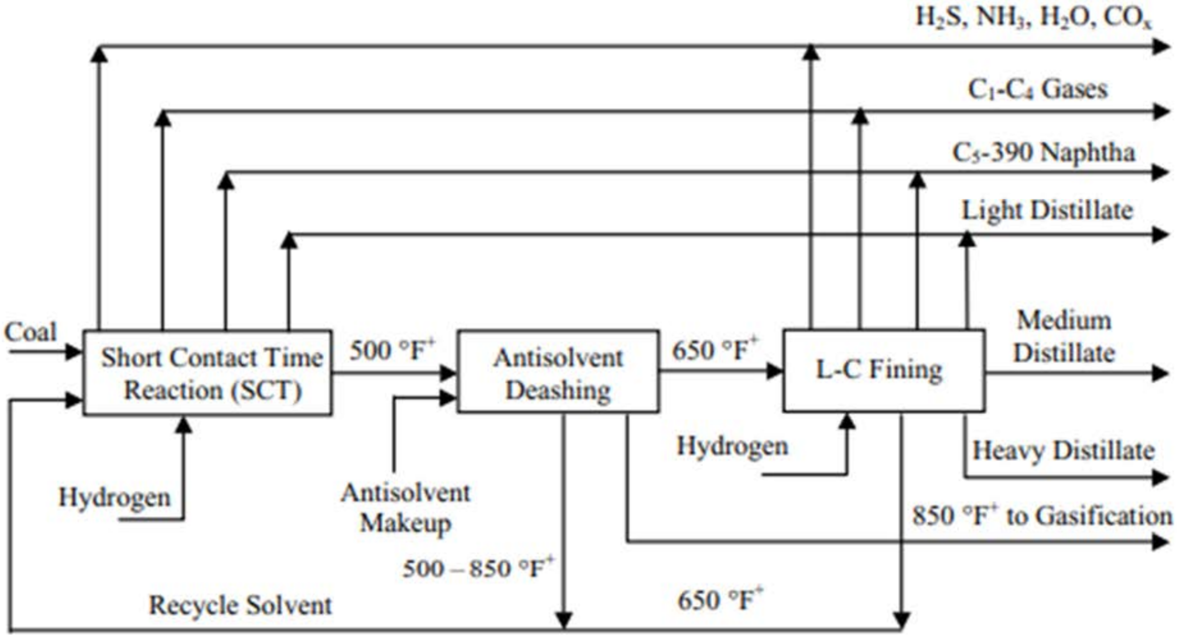

Figure 6.1 Represent the integrated two-stage liquefaction.

The Lummus Antisolvent Deashing (ASDA) process is similar to a petroleum-based deasphalting operation. Distillate at -340°C or -450°C is the net liquid product. The recycle solvent is +340°C atmospheric bottoms hydrogenated. The recycling of these full-range bottoms, including resid, connects the two reaction stages and results in high distillate extraction yields.

The following are some of the Lummus ITSL's features:

1. In the SRC-I process, the SCT reactor serves as a preheater for the dissolver, eliminating the need for a long residence-time high-pressure thermal dissolution reactor.

2. The SCT reactor converted 92% of bituminous coal into mmaf coal and 90% of subbituminous coal into mmaf coal.

3. The consumption of molecular hydrogen gas was nearly zero, and the hydrogen transferred from the solvent was equivalent to 1.2-2.0% of the coal weight. The gaseous hydrocarbon yield from bituminous coal was reduced to 1% and that from subbituminous coal to 5-6%.

4. The SCT resid was more hydrocracking reactive than the SRC-I resid.

5. The LC-Fining second reactor, acting as a hydrotreater (HTR), accomplishes two major tasks: (1) producing almost all of the distillate product and (2) producing recycle solvent capable of supplying the hydrogen required by the SCT reactor.

6. All distillate products were created as a result of the complete recycling of unconverted residue to the first stage.

7. A second-stage HTR temperature of 400°C is sufficient for both hydrogenation and cracking activity.

8. Catalyst deactivation was much slower than in other processes that were run at higher temperatures.

9. The SCT resid was more reactive, not only for distillate conversion but also for heteroatom removal. Product quality outperformed that of the preceding processes. Chevron successfully refined the ITSL products for transportation fuel specifications.

10. Antisolvent deashing (ASDA) was used to remove the ash, which used process-derived naphtha as an antisolvent to precipitate the heaviest components of the residue and solids.

11. The ASDA had the advantage of operating at low pressure (100-1000 psi) and low temperature (260-282°C).

Wilsonville ITSL

Catalytica, Inc. operated the Advanced Coal Liquefaction R&D Facility in Wilsonville, AL, which was sponsored by the DOE, the Electric Power Research Institute (EPRI), and AMOCO and was managed by Southern Company Services, Inc. Hydrocarbon Research, Inc. provided the design for the Hydrotreater (HTR), and Kerr-McGee provided the deashing technology. In 1974, the Wilsonville plant began its operations as a 6-ton/d single-stage plant for SRCI. A Kerr-McGee Critical Solvent Deashing (CSD) unit replaced the filtration equipment used for solids removal from the SRC product in 1978. An H-Oil ebullated-bed hydrotreater was installed in 1981 to improve the recycle solvent and product. To allow operation with close-coupled reactors, a second ebullated-bed reactor was added in the hydrotreater area in 1985 (Figure 6.2).

The efficiency of the ITSL based on distillate productivity per hydrogen consumption is significantly higher than the NTSL result. Lummus improved the ITSL process by increasing distillate yield by placing the deasher after the second stage, with no negative impact on catalyst activity from ashy feed. This improved method is known as reconfigured two-stage liquefaction (RITSL) 6 The process enhancements were experimentally validated at the Wilsonville facility. Higher distillate yield, lower residues, and fewer energy rejects were among the improvements.

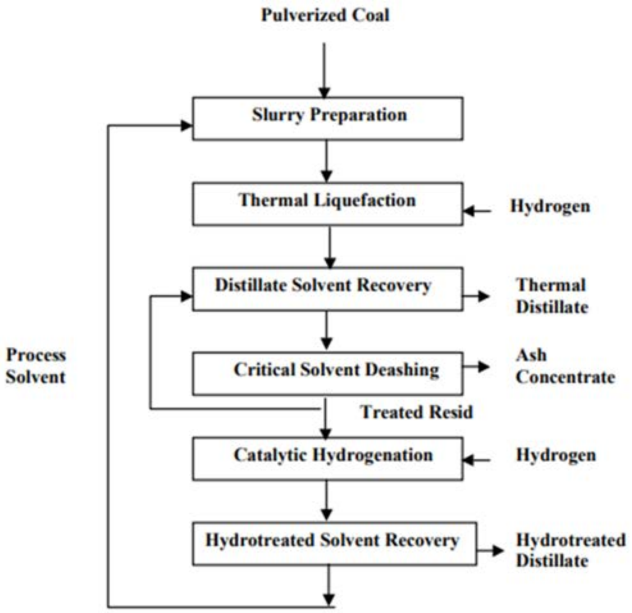

Figure 6.2 Represent the ITSL process.

The two reactors were close-coupled the with deasher placed after the second stage reactor and the fully connected layers operating at roughly the same pressure to minimise holding time between the reactors and eliminate pressure letdown and repressurizing between stages. This improvement was known as close-coupled ITSL (or CC-ITSL). Higher distillate yield, lower residues, and lower energy reject all contributed to the improved results.

HRI's CTSL Process

Hydrocarbon Research, Inc. (now Hydrocarbon Technologies, Inc. (HTI), a division of Headwaters, Inc.) began developing a catalytic two-stage concept in 1982 in order to overcome the drawbacks of H-coal, which is inherently a high-temperature catalytic process. 42 The first-stage temperature was reduced to 400°C to better balance hydrogenation and cracking rates, as well as to allow the recycle solvent to be hydrogenated in situ to aid in hydrogen transfer to coal dissolution. The second stage was run at higher temperatures (435-440°C) to promote resid hydrocracking and the generation of an aromatic solvent, which was then hydrogenated in the first stage. Lowering the first-stage temperature allows for better overall management of hydrogen consumption and lower hydrocarbon gas yieldsdepicts a flowchart of this process.

In comparison to the H-coal process, the HRI CTSL underwent three major changes. The first was the introduction of two-stage processing; the second was the addition of a pressure filter to reduce residue concentration in the reject stream (filter cake) below the 45-50% in the vacuum tower bottoms of the H-coal process; and the third was a change in the catalyst itself. American Cyanamid 1442 B, a cobalt-molybdenum (CoMo)-on-alumina catalyst used in hydrocracking petroleum residues, was used in the H-coal process. In coal liquefaction, hydrogenation must come first, followed by hydroaromatic thermal cracking, whereas in petroleum applications, the opposite is true. As a result of its porosity distribution, which was designed for smaller molecules, the H-coal catalyst was found to be unsuitable. The H-coal catalyst was replaced for CSTL by a nickel-molybdenum (NiMo) catalyst with a bimodal pore distribution. The two-stage catalytic reaction produces a liquid with low heteroatom concentrations and a high H/C ratio, bringing the product closer to petroleum than other coal liquids produced by previous processes. Their improved process is known as the HTI ore process. HTI's proprietary GelCatTM catalyst, a dispersed, nano-scale, iron-based catalyst, is used in the modern version of this process.

Wilsonville CTSL

In 1985, the Wilsonville Advanced Coal Liquefaction Facility added a second ebullated-bed reactor. Since then, the plant has been running in CTSL mode (Figure 6.3). Wilsonville, like ITSL, preferred to do the majority of the thermal cracking in the first reactor and the solvent hydrogenation in the second. As a result, the first reactor was kept at a higher temperature (426-438°C), while the second reactor was kept at a lower temperature (404-424°C).

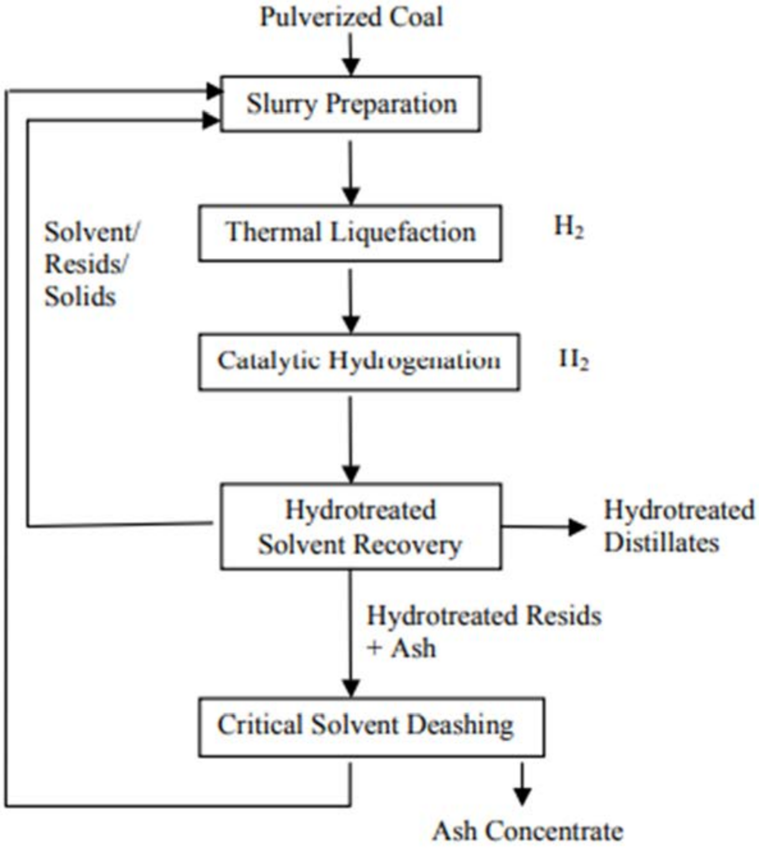

Figure 6.3 Represent the CSTL with a solids recycle at Wilsonville.

where wn, n, and x are the mass fraction, carbon number, and chain growth probability, respectively. this equation can predict the maximum selectivity achievable by a FTS with an optimised process and catalyst.

The chain growth probability can be calculated from a linear story line of log (wn /n) versus n using either the slope (log x) or the intercept, log ((1 - x)2 /x). These predicted values hold true whether the products are only hydrocarbons (paraffins and olefins) or hydrocarbons plus alcohols (a mixture of paraffins, olefins, and alcohols).

Fischer–Tropsch Catalysis

Catalysts with a small value of x (i.e., a lower chain growth probability) produce a high fraction of methane, according to the ASF equation. A high x value, on the other hand, indicates the production of heavier hydrocarbons. The most recent FTS processes aim to produce high-molecular-weight products with very little methane, which are then cracked to yield lower hydrocarbons. There have been numerous attempts to outperform or exceed the ASF distribution in order to produce liquid fuels with yields greater than those expected by the ASF equation.

The FTS employs low-cost iron catalysts. Fusing iron oxides, such as millscale oxides, produces these catalysts. In practise, the catalyst is treated with an alkali salt or one or more nonreducible oxides. There is a wealth of literature data available; however, very few share the same common grounds in their catalyst pretreatment, catalyst ingredients, precursor preparation, and reactor design and configuration, making direct comparison difficult, if not impossible. The removal of wax generated by the reaction is critical in FTS because it can disable the catalytic activity. The SASOL plants meet a large portion of South Africa's fuel and chemical needs.

Produce syngas with low H2/CO ratios (0.6-0.7). Iron is a good water gas shift (WGS) catalyst, whereas cobalt and ruthenium are inactive in the reaction. Because the oxygen in CO is rejected as water gas in the absence of a water gas shift reaction, a syngas with an H2/CO ratio of two is required to produce olefins or alcohols. An H2/CO ratio greater than two is required for the production of paraffins. Water produced in the FTS can react with CO to produce more H2 via the WGS reaction, allowing syngas with a low H2/CO ratio to be used with those same catalysts. This is why the water gas shift reaction is so crucial in the FTS.

Recent research has focused on slurry Fischer-Tropsch (F-T) reactors. Mobil investigated upgrading a total vaporous F-T reactor effluent over ZSM-5 catalyst in the 1980s. Shell announced the SMDS (Shell Middle-Distillate Synthesis) process for producing kerosene and gas oil from natural gas in 1985. The production of long-chain hydrocarbon waxes, followed by hydroconversion and fractionation into naphtha, kerosene, and gas oil, is a two-stage process. UOP defined F-T wax and its potential for improvement. Dow has created molybdenum catalysts with sulphur tolerances of up to 20 ppm. The catalyst system is selective for C2-C4 hydrocarbon synthesis, especially when promoted with 0.5-4.0 wt% potassium. The slurry F-T reactor operating with a finely divided catalyst suspended in an oil reactor medium has been shown to yield high single-pass syngas conversion with low H2/CO ratios when using a precipitated iron catalyst.

A large number of papers on three-phase slurry reactors have been published. The scientific advancement of the F-T synthesis process has aided in the design and analysis of multiphase reactor systems. China and South Africa recently announced a major collaborative project in indirect coal liquefaction. The main entities involved in this venture are Shenhua Group, China's largest coal producer, and SASOL of South Africa. Once completed, the new Chinese plants will have a total annual production capacity of 60 million tonnes of oil.

Conversion Of Syngas To Methanol

Methanol synthesis from syngas is a well-established technology. Because methanol is synthesised from coal as a liquid hydrocarbon using syngas as an intermediate, the coal-to-methanol synthesis processes are classified as an indirect coal liquefaction process. Synthesis gas is created by gasifying coal, gasifying biomass, or steam reforming natural gas. As a result, methanol plant profitability is determined on a case-by-case basis to account for location-specific factors such as energy resources, consumption infrastructure, environmental impact, and capital cost. Methanol plants exist in areas with large reserves of competitively priced natural gas or coal, or where neighbouring chemical plants have large captive uses for product methanol.

The development of methanol synthesis has increased the value of natural gas. At low pressure, conventional steam reforming generates hydrogen-rich syngas. This process, on the other hand, is well suited to the addition of carbon dioxide, which utilises the excess hydrogen and thus increases methanol productivity. From 1991 to 1995, global methanol costs rise by about 8% per year, then by 3-4% per year for the next decade. In 2005, global methanol demand was around 32 million tonnes per year, with growth rates close to or equal to GDP. Because of the recent decline and phaseout of MTBE, regional demand for methanol has suffered in some countries, particularly in North America and Europe.

Nonetheless, global methanol demand is expected to grow at or near the rate of GDP growth. Asia, particularly China, will be the primary driver of demand for methanol and its derivatives. In Asia, average growth rates for methanol are expected to be 3.8%, 4.8% for acetic acid, and 4.4% for formaldehyde. All industrially produced methanol is produced through the catalytic conversion of synthesis gas, the main components of which are carbon monoxide, carbon dioxide, and hydrogen. There are two types of modern commercial methanol processes: vaporphase low-pressure synthesis and solvent low-pressure synthesis. 17,18,20 The former is more traditional and currently dominates the market. This low-pressure vapor-phase process replaced its previous high-pressure technology and is better suited for H_2-rich synthesis gas with a typical H_2/CO ratio of 2 to 3. 17,19 The latter liquid-phase synthesis technology is more recent and better suited for CO-rich synthesis gas with a typical H_2/CO ratio of 0.6 to 0.9. CO-rich syngas is typically produced by modern coal gasifiers,

Methanol productivity can be increased to a certain extent by enriching the synthesis gas with additional carbon dioxide. The optimal carbon dioxide concentration depends on the process type (vapour phase vs. liquid phase), synthesis gas feed compositions, and operating temperature and pressure conditions. However, if there is too much CO_2 in the syngas, it accelerates catalyst deactivation, shortens its lifetime, and produces water, which reduces catalyst matrix stability and results in crystallite growth via hydrothermal synthesis.

Although this is generally true for vapour phase methanol synthesis, it was discovered that a high concentration of CO_2 aids catalyst structural stability by forming $ZnCO_3$ on the original $Cu/ZnO/Al_2O_3$ catalyst. A special catalyst has also been designed to operate under high CO_2 conditions as a different approach. The crystallites of the catalyst are located on energetic stable sites, which reduces migration. This stability also reduces the impact of water formation on the catalyst matrix, which is only marginally affected. This catalyst keeps its properties. Only two of the three reactions are stoichiometrically independent. In other words, the above reaction system's material balance would only require two of the three stoichiometric equations. The chemical mechanism of methanol synthesis over the $Cu/ZnO/Al_2O_3$ catalyst has been a source of debate.

The debate centred on whether methanol is synthesised primarily through CO_2 hydrogenation (Equation 3.1) or through CO hydrogenation. Along with the synthesis reaction, the second companion reaction was naturally at the centre of the debate. The question in this case was whether the water gas shift reaction proceeds forward or backward under normal synthesis conditions over the same catalyst.

Conversion Of Methanol To Gasoline Or Target Hydrocarbons

Methanol, like liquefied petroleum gas (LPG) and ethanol, can be used as a transportation fuel. However, using methanol as an oil products in passenger vehicles would necessitate significant engine modifications as well as significant changes to the lubrication system. Despite having a high octane rating and being an excellent candidate of oxygenated hydrocarbon by molecular formula, methanol's use as a gasoline blending chemical is also limited due to its high Reid vapour pressure (RVP), which is a measure of the affected volatility of blended gasoline. This is one of the reasons why methanol-to-gasoline conversion is appealing. The methanol-togasoline (MTG) process was created by Mobil Research and Development Corporation. The process technique relies on catalytic reactions involving ZSM-5 zeolites. MTG reactions can be expressed as follows:

$$n\ CH_3OH \rightarrow (\ -CH_2-\ )_n + nH_2O$$

The product hydrocarbons can be tailored to fall predominantly in the gasoline boiling range using the shape-selective pore structure of the ZSM-5 class catalysts. Temperature, pressure, space velocity, reactor type, and Si/Al ratio of the catalyst all have an effect on product distributions. Isoparaffins dominate paraffins, while highly methylsubstituted aromatics dominate aromatics. C9 + aromatics are dominated by symmetrically methylated isomers, indicating that the catalyst is shape selective. The C10 aromatics are mostly durene (1,2,4,5-tetramethylbenzene), which has a high octane number but a high freezing point of 79°C. Due to its tendency to crystallise at low temperatures, excessive durene content in gasoline may impair automobile driving characteristics, particularly in cold weather. Mobil's test revealed no drivability loss at -18°C when using a synthetic gasoline containing 4% durene. Mobil also developed a heavy gasoline treating (HGT) process to isomerize and alkylate durene into other high-quality gasoline components.

For the MTG process, three types of chemical reactors were developed: (1) adiabatic fixed bed, (2) fluidized bed, and (3) direct heat exchange. Mobil created the first two, and Lurgi created the third. The adiabatic fixed-bed concept is divided into two stages: (1) the DME reactor and (2) the DME conversion to hydrocarbons. In New Zealand, the first commercial plant with a capacity of 14,500 bbl/d of gasoline was built.

The plant had been operating successfully since its inception in 1985 until its recent closure. The synthesis gas is produced by steam reforming natural gas from the offshore Maui fields. This plant was also successfully operated in New Zealand, reducing the durene content to 2% by weight. The successful operation of MTG in New Zealand was a watershed moment in history because it enabled the chemical synthesis of gasoline from unlikely fossil fuel sources such as natural gas and coal. The sole source of gasoline is no longer petroleum crude. Although the methanol-to-gasoline plant in New Zealand closed in the late 1990s, a major plant complex for methanol-to-olefins is scheduled to open in Nigeria in 2009.

Mobil was working on a fluidized bed MTG concept at the same time. The heat of reaction can be removed from the reactor either directly or indirectly via a cooling coil or an external catalyst cooler. The process research involved a bench-scale fixed fluidized bed, 4 bpd, 100 bpd cold-flow models, and a 100 bpd semiwork plant. MTG process conditions and product yields are typical. During the MTG development, Mobil researchers discovered that by increasing the space velocity, decreasing the methanol partial pressure, and increasing the reaction temperature, the hydrocarbon product distribution can be shifted to light olefins.

C1-C3 paraffins, 4 wt%; C4 paraffins, 4 wt%; C2-C4 olefins, 56 wt%; and C5 + gasoline, 35 wt% were typical yields9 from a 4 bpd operation. Diesel and gasoline can be produced by converting olefins from the methanol-to-olefins (MTO) or F-T processes. Catalytic polymerization with acid catalysts is a standard process used at SASOL to convert C3-C4 olefins into gasoline and diesel (G+D). Using their commercial zeolite catalyst, Mobil recently developed an olefins-to-gasoline-and-diesel (MOGD) process. Lurgi also pioneered its own methanol-to-propylene (MTP) process. Lee and colleagues recently improved an innovative process under the sponsorship of the Electric Power Research Institute (EPRI).

The DTG (DTH, DTO) process is based on the conversion of dimethylether (DME) to hydrocarbon using a ZSM-5 type catalystThis method is based on a novel, cost-effective, single-stage synthesis of dimethylether (DME) from syngas, which generates methanol as an intermediate for dimethylether. By producing DME in a single stage, the intermediate methanol formation is no longer constrained by chemical equilibrium, significantly increasing reactor productivity in terms of total hydrogenation extent. This is especially true for methanol synthesis in the liquid phase. Furthermore, by using DME instead of methanol in the ZSM-5 reactor, the stoichiometric conversion and hydrocarbon selectivity improve significantly due to less water formation and involvement.

The distinction between MTG and DTG is thus in the location of the methanol dehydration reaction step (i.e., DME formation reaction). Methanol-to-DME conversion takes place in the gasoline reactor in the MTG, whereas it takes place in the syngas reactor in the DTG. As a result, methanol is an intermediate of the DTG syngas conversion reactor, whereas DME is an intermediate of the MTG gasoline synthesis reactor. The DTG process has not yet been thoroughly tested on a large scale. To produce an oxygenates mixture rather than methanol, the Topsoe Integrated Gasoline Synthesis Process (TIGAS) employs combined steam reforming and autothermal reforming with a multifunctional catalyst system.

Higher Alcohol Synthesis

C1-C6 alcohol mixtures can be used as transportation fuels on their own or as an additive to gasoline. However, the Clean Air Act prohibits the sale of new unleaded fuels or fuel additives in unleaded fuels in the United States. Exceptions have been made in the form of EPA waivers, and good examples include waivers granted to requests by DuPont, ARCO, Heat, and American Methyl in the late 1970s and early 1980s. Some of the more significant ones that continue to have an impact on the current fuel market in the United States are related to MTBE blending and the use of 10% ethanol in gasoline. Because of the public health and environmental issues raised in a number of states in the United States and Europe. The following are the technical benefits of using C1-C6 alcohol blends with gasoline:

1. Increase in octane number

2. Increased hydrocarbon solubility when compared to methanol-gasoline blends

3. Greater water tolerance than unblended gasoline

4. Improved fuel volatility control

Despite some obvious technological advantages, certain EPA restrictions, particularly volatility specifications (evaporative index [EI] or Reid vapour pressure [RVP]), have imposed significant economic penalties on alcohol blends (other than ethanol), making them difficult to accept by refiners and blenders. In Germany, fuels with higher alcohol blends of around 3-5 mol% have been used for automobile transportation.

Higher alcohol synthesis (HAS) has been used in Germany since 1913, when BASF successfully developed cobalt- or osmium-catalyzed synthesis of an alcohol-and-other-oxygenate mixture at 10-20 MPa and 300-400°C. In 1923-1924, the F-T Synthol process for alcohol mixtures was developed. Higher alcohols were also discovered to be coproducts of methanol synthesis over ZnO/Cr2O3 catalysts, alkalized ZnO/Cr2O3 catalysts, and alkalized Cu-based catalysts. Later, the Synthol process was refined and improved to operate at a lower temperature of 200°C, a medium pressure of 20 MPa, and inexpensive but powerful iron catalysts.

The process was later expanded to include several additional reactor stages with intermediate CO2 removal and gas recycling. Dow Chemical Co. announced a new process for higher alcohol synthesis based on MoS2 catalysis in 1984, and Union Carbide Corporation announced a new process as well. Dow HAS is another name for the Dow Chemical process. Snamprogetti, Enichem, and Haldor Topsoe A/S, on the other hand, developed higher alcohol technology based on alkali-promoted ZnO/Cr_2O_3 methanol synthesis catalysts for high-pressure methanol synthesis (SEHT). This is commonly known as the SEHT HAS process.

CHAPTER 7

COAL AND OIL COPROCESSING

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The simultaneous reaction treatment of coal and petroleum residue, or crude oil, with hydrogen to produce said that liquids is known as coprocessing. More precisely, this technology should be classified as a variation of direct liquefaction. Petroleum liquids were frequently used as liquefaction solvents, primarily during startup or when coal-derived liquids were unavailable. However, some serious thought has recently been given to the processing options of hydrocracking petroleum residue while liquefying coal in the same reactor. Coprocessing has the ultimate goal of cobeneficiation in this sense.

UOP, Inc. received an early coprocessing patent in 1972 for a process that solvent extracts coal with petroleum. Another early coprocessing patent was issued in 1977 to Hydrocarbon Research, Inc. (HRI) for a single-stage ebullated-bed COIL process based on HRI's H-Oil and H-Coal technology. Consol R&D investigated the use of a heavy oil from South Texas for coal hydroextraction but discovered that, even after hydrogenation, the petroleum made a poor liquefaction solvent. 9 The CANMET hydrocracking process for petroleum residues was developed by the Canada Centre for Mineral and Energy Technology (CANMET). They discovered that adding a small amount of coal (5 wt%) to the petroleum feedstock improved distillate product yields significantly. Petro-Canada opened a 5000 bpd plant using this process near Montreal, Quebec in 1985.

To summarise, coprocessing has several potential economic and technological advantages over coal liquefaction or heavy petroleum residua hydroprocessing. Synergies and cobeneficiating effects can be obtained, particularly in the areas of: (1) recycling oil replacement, (2) hydrogen sharing between hydrogen-rich and hydrogen-deficient materials, (3) product aromaticity, (4) demetalation and catalyst life extension, and (5) overall energy performance. 37 Temperatures of 400-440°C, hydrogen pressures of 2000 psig, and alumina-supported cobalt, molybdenum, nickel, or disposable iron catalysts are commonly used in current technology. Various efforts are being made to develop more selective and resilient catalysts.

Coal Slurry Fuel

Coal slurry fuels are made up of finely ground coal that has been dispersed in one or more liquids such as water, oil, or methanol., slurry fuels have the advantages of being easy to handle (similar to heavy fuel oil) as liquid fuel and processing high energy density. Coal slurries have been investigated as a potentially efficient replacement for oil in boilers and furnaces, fuel in internal combustion engines, and, most recently, energy feedstock for coal fines cofiring in utility boilers. Coal slurry is used in countries such as the United States, Russia, Japan, China, and Italy. Coal slurry fuels have been studied since the nineteenth century, but economic constraints have prevented them from becoming a significant energy source. Typically, interest in coal slurry develops whenever regional or short-term oil availability is in doubt, such as during both world wars and again during the 1973 and 1979 energy crises.

During these times, much of the research was focused on coal-oil fuels, which could quickly and easily replace oil or liquid fuel in furnaces and boilers. However, since 1980, research has focused on coal-water slurry fuels (CWSFs) for complete oil replacement in industrial steam boilers, utility boilers, steelmaking, process kilns, and diesel engines. Coal slurry fuels are made up of finely ground coal dispersed in one or more liquids such as water, oil, or methanol. Slurry fuels have the advantages of being easy to handle (similar to heavy fuel oil) as liquid fuel and processing high energy density, Coal slurries have been investigated as a potentially efficient replacement for oil in boilers and furnaces, fuel in internal combustion engines, and, most recently, energy feedstock for cofiring of coal fines in utility boilers. Coal slurry is used in countries around the world, including the United States, Russia, Japan, China, and Italy.

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1. Coal-Oil Mixtures (COM): a coal suspension in fuel oil, also known as coal-oil dispersions (COD).

2. Coal-Oil-Water (COW): a coal-oil-water suspension with less than 10% water in which oil is the main ingredient.

3. Coal-Water-Oil (CWO): a coal suspension in fuel oil containing more than 10% water, in which water is the primary ingredient.

Coal-Water Fuels (CWF), Coal-Water Mixtures (CWM), Coal-Water Slurries (CWS), or Coal-Water Slurry Fuels (CWSF): a coal-water suspension in water.

5. Coal-Methanol Fuel (CMF): a coal suspension in methanol.

6. Coal-Methanol-Water (CMW): a coal suspension in methanol and water.

The CMF and CMW slurries have promising properties; however, the high cost of methanol has effectively ruled them out of further development. COM, which was once actively investigated, has now been shelved due to financial constraints. CWF has been investigated for complete oil replacement in boilers, furnaces, and internal combustion engines, but low oil prices in recent decades have reduced the economic advantage and cooled interest somewhat. CWF derived from waste streams and tailings, on the other hand, was being investigated for cofiring in boilers and furnaces. 16 In the twenty-first century, the comparative economics of coal-water slurry over conventional fuel are undeniably far more favourable. Furthermore, through a long pipeline, CWF provides a valuable mode of coal transportation.

Stability, pumping, atomizability, and combustion characteristics are all important slurry characteristics. The hydrodynamics and rheology of the coal slurry system are controlled by these properties. At pumping shear rates (10-200 sec1) and atomization shear rates, a coal slurry must have a low viscosity (5,000–30,000 sec1). Smaller droplet sizes allow for lower pumping power requirements and increased boiler and furnace efficiencies. For coal slurry pumping, various types of pumps have been developed Understanding dispersed systems is required to comprehend coal slurry hydrodynamics and rheology. Based on particle size, solid-liquid dispersed systems are divided into two types: colloidal and rough systems.

Colloidal dispersion systems contain particles smaller than 1 m in size, whereas coarse particle dispersion systems (suspension) contain particles larger than 1 m in size. Brownian motion prevents sedimentation in colloidal dispersion systems (thermal activity). However, because of the overwhelming gravitational force on large-size particles, suspensions are highly unstable and will tend to precipitate.

particle size distribution

The particle size distribution (PSD) of typical coal slurry fuels is 10-80% smaller than 74 m. (-200 mesh). The PSD of micronized CWF is less than 15 m, and 98% of the particles are less than 44 m. (-325 mesh). This slurry is typically produced by coal benefactors. originates in the removal of mineral matter, primarily pyrites (FeS_2) and ash.Coal sizing is a multistep process that includes coal crushing, pulverisation, and finishing steps. Coal crushing steps include coarse, fine, and ultrafine crushing. Coal crushing reduces the size of the coal to 20-7.6 cm and 5-3.2 cm, depending on the application, and coarse pulverisation reduces the size of the coal to 3.2 mm. Wet or dry grinding can be used to complete the finishing processes. They reduce particle size to 1 mm for coarse grinding, 250 m for fine grinding, and 44 m for ultrafine grinding. Wet grinding is frequently used in slurry preparation to reduce oxidation of the coal, which is normally detrimental to many beneficiation or treatment processes.

According to Stokes' law, reducing the sedimentation velocity requires decreasing the particle diameter, increasing the viscosity of both the dispersing medium, and decreasing the density difference between the solid and liquid phases. However, for optimal slurry processing, high loading at low viscosity is required for transportation and atomization. As a result, the low-viscosity slurry naturally promotes fines sedimentation. Various additives and surfactants have been developed to address this obvious difference with in property requirements of the resulting slurry.

Rheology

The study of a system's response to a mechanical perturbation in terms of elastic deformations and viscous flow is known as rheology. Elastic response is associated with solids in most rheological systems, whereas viscous response is associated with liquids. As a result, a suspension system such as coal slurry exhibits both elastic and viscous responses. These responses in coal slurry depend on the type of coal, coal concentration, PSD, dispersing phase properties, and additive package.

Coal slurries, in general, exhibit non-Newtonian behaviour; however, they also exhibit Newtonian, dilatant, pseudoplastic (shear thinning), and plastic flow characteristics. Newtonian is the most basic response, with a linear relationship between shear stress and shear rate. Slurries typically exhibit pseudoplastic or shear-thinning behaviours, which means that as shear stress increases, the shear rate increases at a slower rate. This is typical of a material with a fragile internal structure that degrades when subjected to shearing stresses. Although the material does not have a yield point, the apparent viscosity decreases with applied stress. Thixotropy is an extension of this behaviour, exhibiting shear thinning that requires significant periods of time to reform the internal structure. The time span can range from a few minutes to several days. Dilatant behaviour is the inverse of shear thinning in that the resistance to flow increases as shear stress increases (Figure 7.1). For flow to begin in plastic behaviour, a sufficient stress, greater than the yield stress, must be applied. Once the suspension yields, the shear stress is proportional to the shearing rate. Yield stress, viscosity, and plasticity are important rheological properties (thixotropy).

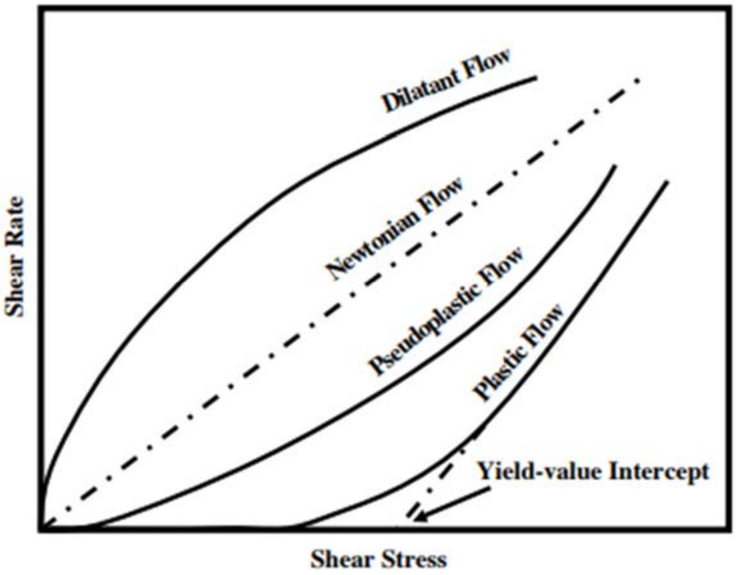

Figure 7.1 Represent the s flow behaviors

where 0 denotes the viscosity of the dispersing phase

r denotes relative viscosity.

viscosity absolute

solids volume fraction

For dilute systems, this equation works well. A number of researchers have developed relations in the form of r = f() to describe higher concentrations, which asymptotically reduce to Einstein's equation at low concentrations. The volume fraction of solids is the only parameter used in modelling these systems. This is referred to as a one-parameter model. This assumes that the particles are inert and that interactions between them are minimal. This equation shows how quickly an increase in the volume fraction of solids,, can reduce the sedimentation rate. However, the increased stability has a negative impact on slurry properties such as viscosity, combustion characteristics, and overall handling. Because of the small dimensions of the particles (most coal particles in slurry are smaller than 50 m), physicochemical forces are important in coal slurry. Although bulk properties such as coal density and water viscosity are important, surface properties have a large impact on slurry properties.

Stability

Slurry stability is divided into three types: sedimentative (static), mechanical (dynamic), and aggregative. A slurry's stability is an important factor in its processability and applicability, which ultimately decide the slurry's value. Slurry stability is affected by density, particle size, solid concentration, surface properties (relative hydrophilic nature), surface charge (zeta potential), coal morphology, and slurrying liquid type. Sedimentative stability refers to a slurry's resistance to gravity. A statically unstable slurry will settle, but the degree of settling decreases as the system becomes more stable. A yield stress in the fluid sufficient to support the largest particle is required for static stability in a fluid. Dynamic stability refers to the stability of a dynamic system. The superposition of mechanical stresses is an example of dynamic stability; pumping and mixing are two examples. Aggregative stability, the third type of stability, is determined by interparticle forces.

Suspension Type

A suspension can be divided into three types: aggregatively stable, flocculated, and coagulated. Repulsion forces prevent particles from adhering to each other in an aggregatively stable suspension. Gravity causes them to settle, resulting in a highly classified and compact sediment with coarse particles at the bottom and fine particles on top. The particles in the flocculated suspension interact weakly to form porous clusters known as flocs. Because of the increased drag forces from the floc structure, they tend to settle slowly. The sediments that form are very loose and take up a large portion of the original wet volume. Mild agitation easily returns the slurry to its original uniform concentrations.

The particles directly interact in the final suspension type, coagulated. Strong attractive interparticle forces encourage the formation of compact and tightly bound clusters that are difficult to break free without significant agitation. These unstable slurries settle quickly and frequently exhibit non-Newtonian behaviour such as thixotropic (time-dependent behaviour), pseudoplasticity (shear thinning), or plastic behaviour.

Interparticle Interactions

The nature of the forces between the molecules governs the properties of coal slurries. In aqueous dispersions, six important particle-particle interactions may exist. 26 A more in-depth examination of these phenomena can be found in the literature.

1. The interaction of electrical double layers (EDL)
2. Attraction van der Waals (VDW)
3. Structural interactions
4. Polymer flocculation
5. Interactions caused by hydration and solvation

Interactions between hydrophobic molecules

When a substance comes into contact with an aqueous polar medium, it acquires a surface electrical charge via mechanisms like ionisation, ion adsorption, or ion dissolution. The surface charge affects the distribution of nearby ions in solution; ions with opposite charges are attractive, while ions with similar charges are repulsive. The EDL is formed as a result of this, as well as the mixing effects of thermal motion. The EDL is made up of a particle surface with a neutralising excess of counterions and, further away from the surface, diffusely distributed co-ions.

The overlap of their diffuse double layers governs the interaction of charged particles. This results in the formation of a potential (Stern potential) at the interface between the Stern plane and the diffuse layer. Unfortunately, measurement device of the Stern potential is impossible; however, the zeta potential (), which relates to the shear plane adjacent to the Stern plane, can be measured Although the zeta6 potential does not always give a good indication of the Stern potential, in some cases an expression such as can be formulated for the repulsive energy (VR) of particle interaction based on surface roughness, shape, and other factors.

When the distance between particles is very small, the attractive force, van der Waals force, encourages particle aggregation. These forces result from spontaneous electric and magnetic polarisations, which produce a fluctuating electromagnetic field within the diffuse solids and aqueous medium that separates the particles. The Hamaker and Lifshitz approaches are two commonly used methods for predicting these forces. The Hamaker method adds the forces between the two bodies pairwise, whereas the Lifshitz method computes the attractive forces directly based on the electro - magnetic properties of the medium. This chapter explains the fundamental ideas of the Hamaker approach, but not the more rigorous Lifshitz method. Hamaker's simpler method for identical spheres is represented by:

$$V_A = -\frac{A_{12}a}{12h}$$

The DVLO (Derjaguin-Landua-Verwey-Overbeek) theory of colloid stability is based on this. 24 depicts the energy interactions for EDL and van der Waals forces. The following total energy curve predicts aggregation at close distances (primary minimum) as well as the possibility of weak and reversible aggregation in the secondary minimum. The shape of the curve is determined by particle size and surface charge. Coarse particles, for example, are more prone to aggregation at the secondary minimum.

Because thermodynamic prognostication may not provide enough information, kinetic effects are important. The stability ratio is used to describe coagulation rates. W is the efficiency of interparticle collisions resulting in coagulations, for two identical particles brought together by diffusion.

$$W = 2\int_0^{\infty} \frac{\exp\left(\frac{V_T}{kT}\right)}{(2+s)^2}\,ds$$

Special cases of interparticle interactions include steric interactions, polymer flocculation, hydration- and solvent-induced interactions, and hydrophobic interactions. The two most important are steric interactions and polymer flocculations. Steric interactions form when cells (usually polymers or macromolecues) are adsorbed at high coverages onto the particle surface. Polymer molecules protrude from the particle's surface into solution. When particles come into contact with one another, the polymer chains overlap and frequently dehydrate, increasing the slurry's stability. Polymer flocculation occurs when a high-molecular-weight polymer has little coverage on the particle surface. Polymers connect the particles and form flocs.

When the interparticle distance is on the order of a solvent molecule, i.e. very short, hydration- and solvation-induced interactions become important. These solvation effects are clearly visible in the structuring of the water near the interfacial surface (with their bound water), which interacts with hydrated ions from solution in aqueous systems. The net effect is increased particle stability or net repulsion as the ions must lose their bound water in order for the approach to continue.

Because the attraction between two hydrophobic particles can increase stability, hydrophobic interactions are analogous to hydration and solvation effects. As a result, hydrophobic particles tend to associate with one another. Hydrophobic forces are stronger than van der Waals forces and have a greater range.

Coal-Water Slurry

Coal-water slurries piqued the interest of technologists initially as a replacement fuel for oil in furnaces and boilers, and more recently for cofiring boilers and furnaces with coal fines. 34 Because of the ease of handling (similar to fuel oil and non-explosive, unlike coal dust), storage in tanks, and injection into furnaces and boilers, CWM and CWSF have received a lot of attention for use as fuel. CWMs typically have extremely high coal loadings of 60-75 wt%, resulting in high energy densities per unit mass. Gas turbines, diesel engines, fluid bed combustors, blast furnaces, and gasification systems are all possible applications. CWM with a lower coal loading of 50% may be used for internal combustion engines, particularly when nonexplosive fuel is required, as in military vehicles and helicopters. However, economic constraints limit the use of minimal additives and lower coal concentrations (50 wt%) in coal slurries for cofiring.

The physical properties of coal slurry are critical in the fuel processing process. A slurry must be stable and have low viscosity at pumping and atomization shear rates. The flow characteristics of coal-water slurry are determined by the following factors: (1) coal physicochemical properties, (2) suspended solids volume fraction, (3) particle size range and distribution (PSD), (4) interparticle interactions (affected by the nature of surface groups, pH, electrolytes, and chemical additives), and (5) temperature. The rheological and hydrodynamic behaviour of coalwater slurries differs depending on the coal. To achieve the desired processability, each coal has a unique package of PSD, concentration, and additives.

The equilibrium moisture content of coal is a parameter that measures how well a coal will slurry, also known as slurry capability (or slurriability). The equilibrium moisture content is a measure (index) of the coal's hydrophilic nature. Proximate analysis can easily determine the equilibrium moisture content of a coal sample. The higher the hydrophilicity of a coal, the more water it can hold and the less likely it is to produce a highly concentrated slurry. The viscosity of the coal-water slurry increases as the coal's hydrophilicity increases. As a result, a hydrophobic coal can more easily form a low viscosity slurry at high solid loadings.

Except for anthracite, conventional high-rank coals (black coal) are hydrophobic due to a lack of acid groups and will form an 80% wt slurry (dry coal weight basis). Anthracite coals are low in reactivity and volatile, resulting in poor ignition stability. Low-rank coals (brown coal) are hydrophilic due to an abundance of oxygen functional groups and will form slurries containing only 20-25 wt% water (dry coal weight basis). 38 These slurries have low concentrations but form nonagglomerating slurries with high reactivities. The difference in coal slurry stability between coal types is caused by the relative balance of acid and base groups on the coal surface. CWMs are loaded to the highest concentration possible at acceptable viscosities. However, viscosity increases with coal concentration (loading), and decreasing viscosity compromises slurry stability.

The slurry's viscosity gradually increases with increasing solid loading until a critical point is reached at which interparticle friction becomes significant. Beyond this point, the viscosity rises sharply until the slurry no longer flows. Surfactants and electrolytes are used to properly stabilise coal-water slurries, i.e. to improve the stability of the coal dispersion. Surfactants are used as dispersants to wet and separate coal particles by lowering the coal-water system's interfacial tension. Surfactants are short-chain molecules that have a hydrophobic group as well as a hydrophilic oxide (nonionic) or charged ionic group (ionic). These molecules bind to the coal particles via adsorption or ionic interaction. Dispersants, in general, are ionic. Sodium, calcium, and ammonium lignosulfates, as well as sodium and ammonium salts of naphthalene formaldehyde sulfonates, are examples of such dispersants.

At hydrophobic sites on the coal particle, ionic surfactants adsorb onto the alkyl groups. This results in a negative charge on the coal particles, which affects the EDL, increasing repulsive forces and preventing agglomeration. Anionic surfactants reduce slurry viscosity up to a critical loading. The coal adsorption sites are saturated at this point, and the remaining surfactant forms micelles in the slurry, resulting in an improved structure and increased viscosity. Nonionic surfactants work in two ways, depending on the nature of the coal. The hydrophobic end of the surfactant is towards the aqueous phase on a hydrophilic coal surface. The water then acts as a lubricant between the coal particles. The second method involves affixing a surfactant to a hydrophilic coal. The surfactant's hydrophilic end attaches to the coal molecule, leaving the hydrophobic end in the aqueous medium. This increases the amount of water near the coal particle's surface, resulting in a hydration layer or solvation shell.

This reduces viscosity and prevents agglomeration by cushioning coal particles. The ionic strength of water in CWM is an important parameter in a slurry's rheological and hydrodynamic properties.

The ionic strength of the water will affect the interaction with coal because coal is a mixture of macromolecular carbonaceous materials and mineral matters rather than a uniformly homogeneous substance. The electrolyte concentration (and its ionic strength) has a significant effect on particle stability against flocculation in a hydrophobic colloidal system dispersed by electrically repulsive forces. With decreasing pH, the cation concentration causes an increase in slurry viscosity. Electrolytes have a significant impact on particle dispersion and thus rheology in CWM with anionic dispersant. Electrolyte addition to a slurry using nonionic dispersants has no discernible effect on viscosity. Although minimal settling is expected in highly concentrated slurries, viscosity-reducing additives increase the settling rate. To stabilise the dispersion, flocculating agents are added, which results in the formation of a gel. Nonionic amphoteric polyoxyethylene polymers, starches, natural gums, salts, clays, and watersoluble polymeric resins are some examples. Polymers have been used to reduce drag, also known as viscosity reduction. Both ionic and nonionic polymer solutions exhibit viscosity reduction, though anionic polymers exhibit a greater reduction.

Coal-Oil Slurry

Coal-oil slurries have been studied for over a century. Interest rates typically peak during periods of high oil prices and scarcity. The most recent interest was fueled by the 1973 and 1979 energy crises, during which enormous effort was expended in finding a quick viable alternative to oil in boilers and furnaces. However, since the mid-1980s, the majority of slurry research has focused on CWM. Except at low coal loadings, where the slurry is Newtonian (provided the oil is also Newtonian), coal-oil slurries exhibit non-Newtonian behaviour, mostly pseudoplastic. The dispersion's viscoelastic properties are affected by coal concentration, PSD, coal type, oil type, and chemical additives. COM's rheological properties are extremely sensitive to coal concentration. At this critical concentration, incremental changes in concentration cause a dramatic increase in viscosity.

There has been research into ultrafine COMs with 95% of particles smaller than 325 mesh (44 m) and slurry concentrations of 50% wt. These slurries are less abrasive, have better combustion characteristics, and contain no additives. However, the grinding cost rises, and coal concentration is usually limited to 50% by weight. Surfactants and polymers are commonly used chemical additives for COMs. Surfactants improve mixture stability by preventing agglomeration and increasing flocculation. Although anionic polymers are more commonly used to reduce drag, cationic polymers are the most effective surfactants for stabilization.

Water is frequently added to coal-oil slurries, forming COW or CWO depending on the water concentration. Water, an emulsification agent, is added to increase the slurry's stability and to save money. Water increases the viscosity of the resulting slurry by forming aggregates and particle bridging, but the combustion properties are mostly preserved.

CHAPTER 8

TRANSPORTATION OF COAL SLURRY

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Coal slurries can be transported using truck and railroad tanks, slurry tankers, and slurry pipelines. Historically, coalwater slurry transportation schemes have received the most attention and development. Despite the fact that all transportation schemes and options have been investigated, couple new processing developments in truck, railroad, or slurry tankers have occurred. In these cases, the slurry stability has been improved to reduce settling during transportation, or the slurry has been dewatered to increase energy density and transportation cost-effectiveness. Coal-water pipeline systems, on the other hand, have been in almost constant development since the 1950s. There are four types of coal pipelines: (1) conventional fine coal, (2) conventional coarse coal, (3) stabilised flow, and (4) coal-water mixture. The particle size of the coal in the slurry differs between thesesystems,

There are only two conventional fine-coal slurry pipelines in the United States. The first was the Consolidation Coal Company's Ohio pipeline, which was built in 1957 and operated for several years until another competitive transportation mode, the unit train, became available. The slurry moved at a moderate speed and contained 50% coal by weight. The Black Mesa pipeline, the second pipeline system built, followed the same basic design as the earlier Consolidation pipeline. The pipeline was built in 1970 and is still in use today. At a 50% coal loading, the pipeline runs at 4-6 mph and is optimised for minimal erosion and settling.

This pipeline's success has had a significant impact on other solid transporting slurry pipelines around the world. Run of mine (ROM) coal is transported at high velocities in coal loadings ranging from 35 to 60%, depending on the coal particle size, in conventional coarse-coal slurry transportation (50–150 mm). The costs of coal slurry preparation are low in this pipeline; however, the energy requirements for pipeline transportation are high. This system is only useful for short distances where other modes of transportation such as rail, barge, truck, or conveyor can be used.

Smaller particles are used to support coarse coal particles in stabilised flow coal slurry systems. Fine coal has a particle size distribution of 0.2 mm, while coarse coal has a particle size distribution of 50 mm. This PSD was used to improve the slurry's stability over long distances of transportation. Coal concentrations of up to 70% by weight are permitted. Because of the particle size, coarse coal is easier to dewater than fine coal. Coal-water mixture pipeline systems are intended for use directly at the final destination, which is most likely in utility boilers and furnaces. Coal concentrations range between 70 and 75 weight percent, with bimodal and polymodal particle size distributions of coal particles smaller than 200 mesh. For slurry stability, CWMs use about 1% surfactants and dispersants. Long-distance pipelines have yet to be investigated (Figuer 8.1).

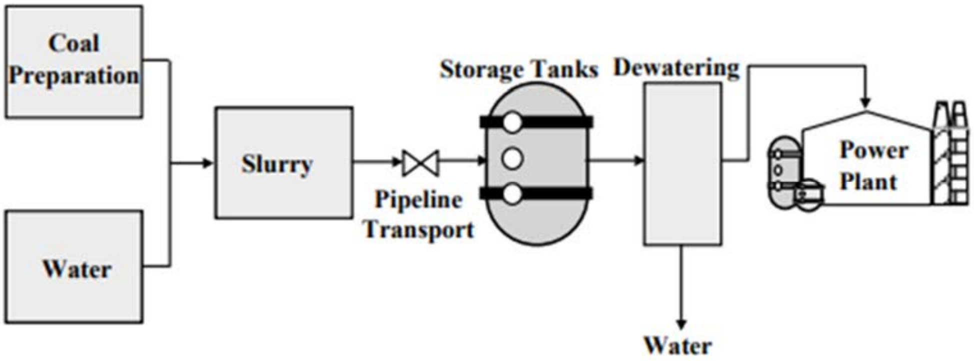

Figure 8.1 Represent the combustion pipeline.

Pipeline carrying coal-water slurry from Black Mesa in northeastern Arizona. The system transports coal from the open pit mine of Peabody Western Coal Company to the Mohave Generating Station, a 1580-MW steam-powered electric generating plant in Laughlin, Nevada. The Black Mesa Pipeline started commercial operations in November 1970 and has transported over 120 million tonnes (as-mined) with a 98% availability factor. The pipeline transports coal at a rate of 570 to 600 M/T (or 0-660 short tonnes) per hour, with a nominal capacity of more than 5 million tonnes (4.5 million tonnes) per year. The Black Mesa Pipeline has aided in the development of other solid transportation pipelines throughout the world, including slurry pipeline transportation of limestone, copper concentrates, iron concentrates, gilsonite, and phosphate.

Environmental Issues

Environmental concerns are crucial in the application of coal slurry fuels. Transportation systems must account for potential leaks and spills associated with slurry handling. To determine the different combustion mechanisms in coal slurry, specifically the mineral matter and sulphur content of the coal, combustion processes must be thoroughly investigated. Spills, leaks, and catastrophic disasters are critical factors in the safe transportation of coal slurries. CWM transportation has been extensively researched for both short and long distances. Water slurries are considered nontoxic and nonhazardous. Historically, when there have been handling accidents in pipeline systems in the United States, no coal cleanup has been required. The coal has been allowed to naturally reenter the ground. CWMs have the distinct advantage of not being easily combustible in an accident.

Many processes will be unable to handle the high sulphur and mineral matter content of coal in the combustion of slurries. As a result, combustion processes in utility boilers and furnaces can sludge, foul, and erode. Other applications, such as cement and asphalt kilns and fluid bed combustors, can easily handle inorganic material increases. The amount of ash that causes fouling in boilers varies depending on the boiler. Sulfur, in both organic and inorganic forms, is an important constituent of coal. Sulfur is a precursor to the formation of ash and can form SOx, which is a precursor to acid rain and has regulated emissions. Coal beneficiation techniques are frequently used to clean coal after it has been ground. Physical and chemical cleaning methods are used in these processes. Physical cleaning methods rely on differences in the density or surface properties of coal and mineral matter. Gravitational separation, froth flotation, selective agglomeration, heavy medium separation, high-gradient magnetic separation, microbubble flotation, and biological methods are examples of physical cleaning processes. Chemical cleaning methods have been extensively researched in the laboratory but are rarely used on an industrial scale. NOx, hydrocarbons (VOCs), and particulate matter are among the other environmentally regulated emissions produced by the combustion of coal slurries (PM). The combustion of coal slurries significantly reduces the amount of hydrocarbon emissions in oil-designed boilers and furnaces. NOx emissions are affected by the nitrogen content of the fuel, the composition of the fuel, the combustion temperature, and the amount of excess air. NOx emissions can be reduced using conventional methods such as low excess air, stage combustion, and low-temperature combustion.

Combustion

Coal combustion in utility boilers (and furnaces) and internal combustion engines was extensively studied during the 1970s and 1980s. The majority of combustion research and development has focused on CWSFs. In general, COM combustion occurs in three stages: (1) droplet heating, (2) volatile matter combustion, and (3) char combustion. For coal, the mass transfer rate of oxygen controls (or limits) the char combustion rate for particles larger than 100 m, while the kinetic reaction rate limits smaller particles. In other words, for large coal particles, the rate-limiting step in the char combustion reaction is the mass transfer rate of oxygen to coal-reactive sites, whereas for smaller coal particles, it is the surface reaction rate. Carbon conversion rates in coal slurry combustion are comparable to fuel oil combustion rates.

The burning characteristics of COM and CWSF differ in that CWSF heat is generated solely by the coal, whereas COM energy is provided by the combustion of both coal and oil. Flame stability, incomplete combustion, erosion, and slagging are all potential issues with CWSF combustion. Atomized droplet size, fuel stability, agglomeration properties, burner swirl, burner throat construction, and preheat air temperature all influence flame stability. Incomplete combustion is caused by insufficient preheating, delayed ignition (water vaporisation), insufficient excess oxygen supply, and agglomeration. Excess velocities of particle-laden gases cause erosion. Inorganic content and slow char particle burnout cause slagging. If CWSF is used in oil boilers and furnaces, the boiler duty is reduced unless the unit is modified. The combustion mechanism for CWSF, which is similar to that of pulverised coal but includes an additional stage of water evaporation. The droplet of coal slurry is injected into a hot gas stream and quickly dries. While undergoing plastic deformation during pyrolysis, the particles in the droplet agglomerate due to surface forces and become tightly bound. Ignition takes place, and devolatilization results in fragmentation. During burnout, the char fragments even more.

The energy absorbed to vaporise the water lowers the temperature of the flame. The atomization of the slurry has a significant impact on the combustion efficiency. Fine atomization accelerates evaporation by increasing surface area and decreasing agglomerate size. Smaller droplets result in more stable flames and higher carbon burnout. Coal-water slurry firing of conventional boilers has been done for a long time with few operational issues. The boilers were successfully started, operated reliably and safely, and met emission standards. The thermal efficiency was 79% and the combustion efficiency was 95%. However, in order to increase efficiency to over 99%, costly modifications must be made, and maintenance schedules are expected to be up to 6 times per year.

Coal was previously only used in external combustion engines (Rankine cycles). Attempts at coal utilisation on large-bore diesel engines have been investigated since the development of the diesel engine in the 1920s. Fuel introduction, combustion efficiency, and engine wear were among the issues that could not be resolved at the time, and the work was halted.

The CWSF investigation has rekindled interest in coal-fired internal combustion engines. Recent feasibility studies have revealed that slurry engines have thermal efficiencies comparable to oil engines, and the use of new materials has reduced the erosive effects. The presence of water in the fuel allows NOx emissions to be controlled. Although hydrocarbon and CO emissions are low, CO_2 emissions are higher than oil due to coal's high carbon content. Particulate traps can easily handle the generated particulates.

The challenges of using CWSF in diesel engines are fuel injection (atomization), ignition, erosion, and corrosion.The efficiency of a fuel injection system is determined by slurry properties, combustion chamber layout, fuel compatibility, ignition delays, and erosion. The initial ignition of CWM is difficult because the water in the coal must first be evaporated. Operating combustion temperatures are higher, with 1000-1100 K being the optimal range. This is to reduce the ignition delay caused by water evaporation and the slower burning of coal. Erosion of parts in the injection system and cylinders is a major concern for engine longevity. Engine wear is six times greater in a CWM-fired engine than in a diesel-fired engine, but it can be reduced to twice as much with special alloys and redesigned parts. These results bode well for the success of efforts to run an internal combustion engine on CWSF.

Coal-water fuels have seen the most recent process development. Australia, Canada, China, Italy, Japan, Sweden, and the United States have all built coal slurry facilities. Japan, China, and Russia have been the most active. China has constructed a number of slurry production facilities and boiler units. Japan has conducted extensive research and technological development on slurry processes, and several boilers have been converted. Russia has constructed a number of pipelines, manufacturing facilities, and boilers. Since 1987, a group of Australian companies led by Ube Industries, Nissho Iwai Corp., and Coal & Allied Industries has been developing the production, transportation, and marketing of CWM from Australia to Japan.

China and Japan conducted the first bilateral trade in coal slurry in 1991. Yanzhou Coal Mining Bureau, Nisshon Iwai Corp., and JWG Corporation built a coal-water slurry plant in Rizhao, Shandong province. The plant has a yearly capacity of 250,000 tonnes. The coal is mined and then transported to Rizhao by train. The coal is converted into CWM before being shipped to an overseas terminal. The CWM is transferred to coastal shipping and then to end users once it arrives at the relay terminal. The production, transportation, and combustion of coal slurry have all been technically straightforward. The most promising application for CWM in the United States may be the use of coal fines in cofiring boilers. Over 40 million tonnes of coal fines are discarded into slurry ponds in the United States each year, with an estimated 2.3 billion tonnes of coal fines in ponds in 1994. With the increased demand for cleaner coal, the production of coal fines (-100 mesh) has increased over the years. Due to increased demand for high-quality coal (often beneficiated), 20-50% of coal mined is being rejected as coal fines. The environmental impact of coal fines includes nonproductive land use, aesthetic loss, the risk of slides, dam failure, significant permitting costs, and potential water pollution.

GPU Energy (PENELEC), New York State Electric and Gas Corporation (NYSEG), Pennsylvania Electric Energy Development Authority (PEEDA), Pennsylvania Electric Energy Research Council (PEERC), and the Electric Power Research Institute (EPRI) recently commissioned a study into the use of CWM developed for coal fines. The project looked into both laboratory-scale and full-scale cofiring of a 32-MW boiler.

CWM will alleviate coal-handling issues and eliminate the need for expensive dryers and their associated environmental risks. CWM will also eliminate the need for oil to be added at startup to stabilise the combustion. Furthermore, by reducing the equipment load, the pulverizer's equipment life will be extended. Because CWM from coal fines is a lower-cost fuel, it has the potential to stabilise the cost of fuel to the boiler, and the fuel ratio can be controlled up to   In terms of the environment, the addition of coal slurry reduces NOx emissions.

To be economically competitive, the lowest-cost slurry must be developed, which may result in a "low-tech slurry," i.e., one lacking stabilisers, dispersants, or the need for additional grinding. This slurry can be made from coal pond fines, a fine coal fraction of existing coal supplies, or in the future, using advanced coal technologies to deep-clean fine coal. The slurry was tested with solid loadings ranging from wt% coal, and the results showed excellent handling and storage properties. Slurry made from coal fines, on the other hand, is highly variable. PSD, ash level, and oxidation extent all influence slurriability. Therefore, slurry preparation can vary from a minimal processing to a significant processing. Minimal processing is from coals derived from wet, fine coal that has been cleaned. Significant processing can come from coal fines that have high ash content and oxidation levels. High oxidation makes the coals more wettable through oxygen bonds, which in turn increases the viscosity and stability of the slurry. Typically, weathered coals are more oxidised.

Coal slurry development is once again adjusting to process economics. Since the mid-1980s, COM, which was once the most researched slurry, has become uneconomical, and development has shifted to CWM. Slurry development on production, pipelines, and combustion continues in regions where coal is abundant but transportation is lacking, such as China and Russia. In other places, such as Japan, where natural resources and storage space are scarce, the ease of transportation made possible by CWM is now being used. Coal utilisation is now the focus of coal slurry development in the United States. CWM allows for the use of more coal after beneficiation and greatly reduces the environmental liability associated with discarded coal fines. Internal combustion engine development of coal slurry continues in injection systems, atomizer design, and construction materials. The development of coal slurry processes will continue, and it may be poised to become a major source of coal energy.

Liquid Fuels from Natural Gas

The gaseous mixture found in petroleum reservoirs is known as natural gas. It is primarily composed of methane. This gas, like petroleum and coal, is derived from the remains of plants, animals, and microorganisms that lived millions of years ago. Natural gas may be considered uninteresting in its pure form because it is colourless and odourless. This gas is a combustible mixture of hydrocarbon gases that includes, in addition to methane (C_2H_6), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and pentane (C_5H_{12}). Its composition, however, varies greatly. It is combustible and produces energy when burned. Natural gas, on the other hand, burns cleanly and emits fewer potentially harmful byproducts into the atmosphere than other fossil fuels. Liquid fuels, on the other hand, are typically more complex hydrocarbon mixtures than natural gas. Thus, for the purposes of this chapter, the term liquid fuel refers to any liquid that can be used in an internal combustion engine. This definition also includes diesel and all types of aviation fuels.

Natural gas can also be converted into alternative fuels. Alternative fuels include methanol, ethanol, and other alcohols; mixtures of methanol and other alcohols with gasoline or other fuels; biodiesel; fuels derived from biological materials (other than alcohol); and any other fuel that is not primarily derived from petroleum. Liquid fuels derived from sources other than petroleum include those derived from tar sand (oil sand), bitumen, coal, oil shale, and natural gas.

These so-called synthetic liquid fuels (termed synfuels) have properties similar to those of petroleum-derived liquid fuels, but differ in that the constituents of synfuels do not occur naturally in the raw materials used to make them (Han and Chang, 1994). Thus, synfuels are liquid fuels derived from sources other than natural crude petroleum. Throughout much of the twentieth century, the emphasis was on liquid products derived from coal upgrading or from the extraction or hydrogenation of organic matter in coke liquids, coal tars, tar sands, or bitumen deposits. Natural gas's potential as a source of liquid fuels has only recently been recognised, and attention is now focused on this new source of liquid fuel.

Petroleum shortages are expected, indicating that alternative sources of liquid fuels are required in the twenty-first century. Although such sources (for example, natural gas) exist, the exploitation technologies are not as mature as those for petroleum. The possibility of converting natural gas into valuable chemicals, particularly liquid fuels, has been known for many years. However, the high cost of steam reforming and the partial oxidation processes used to convert natural gas to synthesis gas has hampered natural gas's widespread use. Tar sand (also known as oil sand or bituminous sand) and coal are two other viable sources of liquid fuels.

Natural gas, which typically contains 85-95% methane, has long been recognised as a plentiful and environmentally friendly alternative feedstock to crude oil. At the moment, the rate of discovery of proven natural gas reserves is increasing faster than the rate of production of natural gas. Many large natural gas deposits are found in areas with abundant crude oil resources, such as the Middle East. Huge reserves of natural gas, on the other hand, are found in many other parts of the world, providing oil-deficient countries with a plentiful energy source. It is often located in remote areas far from any consumption centres, and pipeline costs can account for up to one-third of the total cost. Thus, there are tremendous strategic and economic incentives for gas conversion into liquids, especially if it can be done on-site or near the wellhead to reduce transportation costs.

Nonetheless, despite its diminished prominence, coal remains a viable option for the future production of liquid fuels. World petroleum production is expected to level off and then decline, and despite the apparent surplus of natural gas, production is also expected to fall. The gasification of coal into synthesis gas (syngas) is used in the same way that natural gas steam-reforming technology is used to synthesise liquid fuels. It is more important, however, to maximise the use of available natural gas reserves and the conversion of natural gas to liquid fuels. Liquid fuels have the inherent advantage of being easier to store, transport, and measure than natural gas. They are also easier to process or clean using chemical and catalytic methods, and they are more compatible with 20th-century fuel infrastructures because most fuel-powered conveyances are designed to operate only with relatively clean, low-viscosity liquids. As a result, producing synfuels from alternative feedstocks requires adjusting the hydrogen-carbon ratio to the desired intermediate level.

Occurrence And Resources

Natural gas can be found in the earth's crust's porous rock alone or in conjunction with petroleum accumulations (Speight, 1993 and references cited therein). In the latter case, the gas forms the gas cap, meaning the mass of gas trapped between the liquid petroleum and the petroleum reservoir's impervious cap rock. When the pressure in the reservoir is high enough, natural gas can dissolve in the petroleum and be released during drilling operations.

It is a fossil fuel produced, like petroleum, by the transformation of the remains of plants, animals, and microorganisms that lived millions of years ago. Natural gas is abundant in North America, yet it's a nonrenewable resource that is essentially irreplaceable. As the use of natural gas grows, it is critical to understand the availability of natural gas supply. The 2003 British Petroleum (BP) report shows current estimates of global natural gas availability (BP Statistical Review of World Energy, 2003). As a result, it is estimated that a large amount of natural gas is still underground.

However, it is critical to compare the various methodologies and classification systems used in such estimates, as well as to delve into the assumptions behind each study in order to gain a complete understanding of the estimate itself, with a particular focus on proven and potential resources. These estimates are constantly being revised. Because of new technology and increased knowledge of specific areas or reservoirs, these estimates are constantly changing. The fact that there are no universally accepted definitions for the terms used differently by geologists, engineers, and resource accountants complicates matters even more. The majority of the natural gas that exists in North America is concentrated in a few geographical areas, or basins. Natural gas reserves are highest in states located on top of a major basin. Natural gas reserves in the United States are mostly concentrated around Texas and the Gulf of Mexico.

Natural Gas Liquids

The term natural gas liquid, also known as natural gasoline, refers to the hydrocarbons with a higher molecular weight than methane that are found in natural gas This category includes mixtures of liquefied petroleum gas, pentanes, and higher-molecular-weight hydrocarbons. It is important not to confuse natural gasoline with straight-run gasoline (also incorrectly referred to as natural gasoline), which is gasoline that has been distilled unchanged from petroleum.

Conversion Of Natural Gas To Liquids

Once the synthesis gas is produced, two routes can be used to convert natural gas to liquid fuels using indirect technology ; both routes have been commercialised. One route involves using Fischer-Tropsch technology to directly or indirectly produce liquid fuels. The other option is to produce methanol, which is then converted into liquid fuels.

In general, steam reforming to produce syngas is the proven technology for upgrading methane (carbon monoxide plus hydrogen). When such a gas mixture is converted to liquids, it produces liquid fuels free of heteroatom compounds containing sulphur and nitrogen (except for a trace amount). The highly publicised direct methane conversion technology involves the oxidative coupling of methane to produce higher hydrocarbons such as ethylene. These olefin products (i.e., hydrocarbons with the -C=Cfunction) can be converted to liquid fuels using catalytic oligomerization processes, which are currently used in the petroleum and petrochemical industries (Speight, 1999 and references cited therein). A second trend in synfuels is an increased focus on oxygenate compounds as alternative fuels as a result of growing environmental concern about the use of fossil-based fuels. Because the environmental issues associated with the use of oxygenates such as methanol, ethanol, and methyl tert-butyl ether (MTBE) are not fully understood or resolved, the environmental impact of these compounds must be carefully considered.

Thus, using natural gas to produce synfuels and chemicals provides a clean and cost-effective alternative to the conventional fuels and chemicals. For chemical production, the most promising scenarios involve producing olefins, as well as the resulting polymer products, in a remote location and shipping them to developed markets (Figure 8.2).

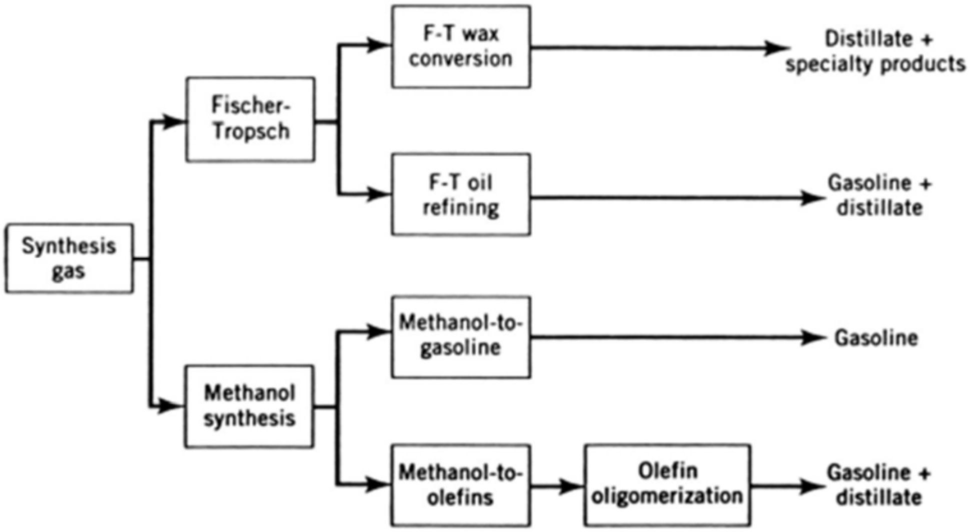

Figure 8.2 Represent the Natural gas to liquid fuels.

The world has approximately 5500 trillion cubic feet (tcf) of proven natural gasreserves (ope, and Asia. Indirect coal liquefaction and natural gas conversion to synfuels are defined by technology that includes an intermediate step to generate syngas. Several technologies, including gas-to-liquids (GTL), methanol-to-gasoline (MTG), methanol-to-olefins (MTO), methanol-to-propylene (MTP), olefins-to-gasoline and distillates (MOGD), dimethyl ether (DME) processes, large-scale methanol processes, and power generation from methanol, have been and continue to be evaluated by various companies.

Shell's (middle distillate synthesis process [MDS process]) and Sasol's commercially proven technologies for producing middle distillates via GTL processes show great promise for fuel alternatives and higher-value products. Because of their high concentration of normal paraffin components, Fischer-Tropsch naphtha and gas oils produced by various GTL processes are appealing for steam-cracking applications. Because of their high paraffinic content, Fischer-Tropsch liquids can be cracked at extremely high severities that are not typical for conventional feedstocks. When compared to conventional naphtha-cracking yields, Fischer-Tropsch naphtha has a higher selectivity to ethylene and a lower selectivity to heavier products like butanes.

Syngas Production

syngas is a carbon monoxide (CO) and hydrogen (H_2) mixture produced by steam-reforming natural gas. O_2 (CO_2) is almost always produced in addition.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

This gas is a critical precursor in the production of methanol, hydrogen, ammonia, and other products. The Fischer-Tropsch process, in particular, can convert methane to syngas and gasoline from this mixture. Syngas produced using current methods accounts for roughly 60% of the total cost of converting natural gas to gasoline. As a result, natural gas is an excellent option for a plentiful alternative energy source

The growing number of hydrogenation (hydrocracking and/or hydrotreating) processes in refineries, combined with the need to process heavier oils, which require significant amounts of hydrogen for upgrading, has resulted in vastly increased demand for this gas. A portion of the hydrogen demand can be met by recovering hydrogen from catalytic reformer product gases, but other external sources are required). The majority of external hydrogen is produced through steam-methane reforming or oxidation processes. Other processes, such as steam-methanol interaction or chlorine dissociation, can also be used as hydrogen sources. Water electrolysis yields high-purity hydrogen, but the power costs may be prohibitiveSteam-methane reforming is a continuous catalyst process that has been used for several decades to produce syngas and, in some refineries, hydrogen. The formation of carbon monoxide and hydrogen from methane and steam is the primary reaction.

CHAPTER 9

FISCHER–TROPSCH PROCESS

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The world's hydrocarbon resources are not distributed evenly. A significant portion of known reserves are located in remote areas far from areas of high consumption. The transportation of liquid fuels from source to consumer requires a large and flexible infrastructure. When natural gas deposits in remote locations must be exploited, transportation becomes a major challenge, especially if geography, economics, or a combined effect of both precludes the possibility of a pipeline. The production of synfuels from natural gas (via syngas) can take one of two routes: (1) the hydrocarbon route or (2) the methanol route. Both routes are commonly known as the Fischer-Tropsch synthesis (Friedel and Anderson, 1950). For both routes, the first step is to convert natural gas into syngas (a mixture of hydrogen and carbon monoxide with some carbon dioxide). The proportions of these components in the mixture vary depending on the individual synthesis process chosen, as well as the product slate desired. The typical values of the principal characteristic, the H2-to-CO ratio, for various processes range from less than one to nearly three. Because of the wide range of H2-to-CO ratios required for the various synthesis processes, considerable effort is required to match the syngas generation and synthesis processes in order to achieve the best overall conversion rate. Furthermore, varying amounts of pure hydrogen may be required for hydrogenation of the synthesis's crude product.

General Process Description

Fischer-Tropsch synthesis is a well-known process for converting syngas to synfuels and chemical raw materials. The process's raw materials consumption is versatile, in that it can use any type of coal, natural gas, or similar types of carbon-containing feedstock as its material, and the product distribution can also be changed. The rise in mineral oil prices has fueled intense efforts to commercialise the Fischer-Tropsch process. Even though the Fischer-Tropsch reaction was discovered 90 years ago, the details of the reaction and process are still unknown.

Synfuels derived from the Fischer-Tropsch process are now more expensive than hydrocarbon fuels derived from natural oil. However, under certain conditions and over the next century, the economics of the process may improve. The process merits special attention in areas where (1) coal reserves are important and available at a lower cost, and (2) natural gas is abundant. In the long run, coal-based hydrocarbon synthesis will outnumber oil production.

Syngas (a mixture of CO and H_2) can be produced by steam-reforming or gasification processes from coal or coke, natural gas, or other carbon-containing feedstock (as described earlier). Catalysts are used in the synthesis of hydrocarbons. To increase the surface area of the catalyst, metals such as ruthenium (Ru), iron (Fe), and cobalt (Co) are typically deposited on an inert support such as silica, alumina, or aluminosilicates. Most commonly, promoters are added to improve catalyst properties or selectivity. P = 10-40 bar and T = 200-300°C are typical reaction conditions for the Fischer-Tropsch process.

Commercial Processes

Tubular steam reforming, catalytic autothermal shaping, and noncatalytic partial oxidation are the three main industrially proven processes.The methane-steam reaction occurs over a catalyst in an externally heated tube in tubular steam reforming. To prevent carbon formation in the catalyst, a large amount of steam is required. This causes the carbon monoxide shift reaction to shift to the right, producing a hydrogen-rich syngas. Outside the tubes, the heat is primarily supplied by the unfavourable complete combustion reaction of methane to carbon dioxide and water.

Oxygen is added to the feed in catalytic autothermal reforming. The methane-oxygen partial oxidation state partially meets the heat requirement for the methane-steam reaction , resulting in a lower hydrogen-to-carbon-monoxide ratio in the syngas. Significant amounts of steam, as in tubular reforming, are required to suppress carbon formation. The absence of metallurgical limitations of a steam reformer's catalyst tubes allows for higher operating temperatures, reducing methane slip. The carbon monoxide shift equilibrium is also more favourable to carbon monoxide at these higher temperatures than in the tubular steam reformer. The reaction of methane with oxygen is dominant in noncatalytic partial oxidation. Because there is no catalyst, the process is tolerant of a small amount of carbon formation and can operate at higher temperatures. As a result, partial oxidation can be carried out without the addition of any steam, and the resulting syngas is high in carbon monoxide.

The art of selecting the right syngas generation process (or combination of processes) entails ensuring the correct gas specification as required by the selected synthesis while also minimising certain inherent inefficiencies of the individual processes. In the case of tubular reforming, the inherent inefficiency is due to the use of external complete combustion, which necessitates an expensive heat recovery train while still resulting in significant losses in the stack gas. The inefficiency in autothermal reforming and partial oxidation is due to the energy required and the investment in the oxygen plant. Lurgi GmbH is currently designing and supplying syngas production units for two major synfuel projects, one based on Sasol's Synthol process and the other on Shell's SMDS synthesis . Because the hydrogen to carbon monoxide ratios required by the two processes differ significantly, different syngas production routes have been chosen.

Sasol has been using the Synthol process on a commercial scale since the 1950s, and it has evolved over time. The Arge Process used low temperatures, medium pressures, and a fixed catalyst bed in the beginning. This process primarily produced a linear paraffin wax, which was later used as a petrochemical feedstock as well as a transport fuel. Until the 1950s and 1960s, this was the only method available. Following that, the Sasol Synthol process was developed, which involved higher temperatures and medium pressures, but used a circulating fluidized pillow to produce light olefins for chemical and gasoline components. This procedure was recently upgraded to the Advanced Synthol procedure. The Sasol slurry-phase reactor, an integral part of the Sasol slurry-phase distillate (SSPD) process, is the most recent advancement in Fischer-Tropsch technology. It conducts the synthesis reaction at low temperatures (200-250°C) and pressures. Hot syngas is bubbled through a liquid slurry of catalyst particles and liquid reaction products. Heat is removed from the reactor via coils within the bed, resulting in the production of steam. The reactor's liquid products are removed, and the liquid hydrocarbon wax is separated from the catalyst. The gas streaming from the reactor's top is cooled in order to recover light hydrocarbons and reaction water. The Sasol slurryphase technology has undergone several developments, the majority of which have been focused on catalyst formulations. Initially, an iron-based catalyst was used, but more recently, a cobalt-based catalyst has been used, resulting in higher conversion.

The Shell middle-distillate synthesis (SMDS) is a two-step process that involves the heavy paraffin synthesis and Fischer-Tropsch synthesis of paraffinic wax (HPS). In the heavy paraffin conversion (HPC), the wax is hydrocracked and isomerized (in the presence of hydrogen) to produce a middle-distillate boiling-range product. Wax is maximised in the heavy paraffin synthesis stage by using a proprietary catalyst with high selectivity towards heavier products and a tubular, fixed bed reactor. In a trickle flow reactor, a commercial hydrocracking catalyst is used in the heavy paraffin conversion stage. The heavy paraffin conversion step enables the production of narrow-range hydrocarbons that would not be possible using traditional Fischer-Tropsch technology.

The products are primarily paraffinic, free of sulphur, nitrogen, and other impurities, and have excellent combustion properties. The extremely high cetane number and smoke point indicate clean-burning hydrocarbon liquids with low exhaust emissions. This method has also been proposed for the manufacture of chemical intermediates, paraffinic solvents, and extra-high viscosity index lube oils. The Lurgi combined reforming process was designed originally for large-scale methanol production, and it is this application that is discussed here. It is suitable as a building block for the MTG or the MOGD process in the context of liquid fuel production. Carbon dioxide must be removed from the system before the high-pressure Synthol process can begin (Figure 9.1). Depending on the quality of the natural gas feedstock, the conventional tubular steam-reforming process used for methanol syngas production produces a hydrogen to carbon monoxide ratio of more than 4 and a stoichiometric ratio of 2.6-2.9 (i.e., a hydrogen-rich gas).

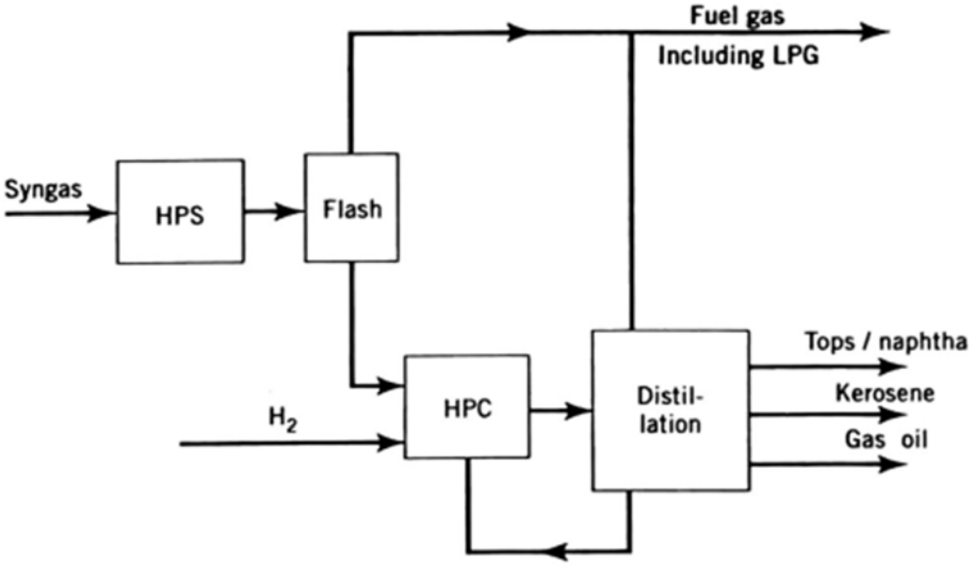

Figure 9.1 Represent the Shell middle-distillate synthesis (SMDS) process.

Autothermal reforming or partial oxidation generates carbon-monoxide-rich gases with hydrogen-to-carbon-monoxide ratios ranging from 1.5 to 3.5 and a stoichiometric number of around 1.8. The tubular primary reformer processes approximately half of the feed. The other half, along with the effluent from the primary reformer, is autothermally reformed with pure oxygen in the secondary reformer. Aside from matching hydrogen-rich and carbon-monoxide-rich process steps to achieve an optimal stoichiometric ratio, the combined reforming process has several other advantages, including the following:

The temperature of the secondary reformer, which is not subject to the same tube metallurgy limitations as the tubular reformer, governs the overall methane slip of the reforming process. As a result, the combined process can provide lower methane slip.

Less optimised quality syngas is required per tonne of methanol, lowering both the syngas compressor load and the capital cost of the synthesis unit.

The primary reformer operating temperature no longer needs to be chosen to minimise methane slip. The reformer can also be used in mild weather. The increased operating pressure allows the syngas compressor load to be reduced even further.

The reduced throughput through the primary reformer, combined with the lower operating temperature, results in a tubular reformer that is approximately 25% the size required for the single-stage process. This reduces the earlier mentioned stack gas losses by the same amount.

The Shell Gasification Process (SGP) is a much older process, with the basic development occurring in the 1950s. Over the last 50 years, more than 150 units have been constructed. Depending on the steam addition rate, the unit produces synthesis gas with a hydrogen-to-carbon-monoxide ratio of 1.7-1.8 and a carbon dioxide content of 1.7-3 volume percent from natural gas feedstock.

The gas feed is preheated in the unit with the raw gas to about 380°C for desulfurization before being fed to the SGP reactor with oxygen. The partial oxidation reaction occurs in the refractory-lined reactor at around 1300-1400°C. The hot gas's sensible heat is used to generate high-pressure steam, with or without superheat as needed. Small amounts of soot are produced by the noncatalytic partial oxidation reactor and are washed away in a scrubber. The carbon is concentrated in the reaction water, which is then discharged to be treated as wastewater.

When the syngas quality is compared to that produced by combined reforming, the SGP process has a significantly lower hydrogen to carbon monoxide ratio of 1.86 versus 3.14 for combined reforming, making it a better match than, for example, the SMDS process. In this case, the amount of natural gas required to produce syngas is approximately 3.5%. These benefits may be offset by increased oxygen requirements. The inherent lack of selectivity is a feature shared by all Fischer-Tropsch processes. The actual selectivity is determined by the desired product slate, the catalyst, and the operating conditions. However, significant amounts of gaseous hydrocarbons, including methane, are produced in all cases.

In theory, it is preferable to recycle these gaseous hydrocarbons in order to produce more syngas. On the other hand, inert gases, primarily argon and nitrogen, must be purge. Another aspect of selectivity that must be acknowledged is that a proportion of higher-molecular-weight products, such as waxes, are produced and may require hydrotreating to be converted to a saleable product. The Syntroleum process is a low-cost refinement of GTL technology that has been used for decades. One significant advantage is that the process uses compressed air rather than pure oxygen to facilitate the conversion reaction, significantly lowering capital costs and vastly improving process plant safety.

The Syntroleum process is comprised of three major reaction steps: (1) natural gas is partially oxidised with air to produce syngas, (2) syngas is then reacted in a Fischer-Tropsch reactor to produce liquid hydrocarbons of varying chain lengths, and (3) the higher-boiling fraction of the products is separated and hydrocracked to produce transportation fuels. Middle distillates of naphtha, kerosene, diesel, and other hydrocarbon-based products are used to produce synfuels.

There are three key steps in the ExxonMobil AGC-21 process:

1. In the first step, syngas is generated by having to contact methane with steam and a limited amount of oxygen in a high-capacity catalytic reactor.

2. In the second step, hydrocarbons are synthesised at high alpha using a Shulz-Flory distribution in a novel slurry reactor with new, highproductivity catalysts operating at high levels of syngas conversion. The full-range, primarily normal paraffin product contains 650°F+ waxy material that is solid at room temperature and melts above 250°F, making it unsuitable for pipelining or transport in conventional crude carriers.

3. The final step, accomplished with proprietary catalysts in a packed bed reactor, converts wax to high-quality liquids that make excellent feeds for refineries and chemical plants, and directly marketable products in some instances, such as lube basestocks or specialty solvents.

The chemistry of each step is straightforward, yet becomes much more complex as processes go to high yield and selectivity. The ratios of oxygen, methane, and steam are carefully controlled to produce syngas (carbon monoxide and hydrogen) at stoichiometric proportions of approximately 2.1 to 1, hydrogen to carbon monoxide.

Methanol is produced catalytically from syngas and by-products, such as ethers and formic acid esters, and higher hydrocarbons, are formed during side reactions and are found in the crude methanol product. For many years, coal was used to produce methanol, but after WWII, low-cost natural gas and light petroleum fractions replaced coal as the feedstock. Following that, the Mobil MTG process is one of the most significant developments in synfuels technology since the discovery of the Fischer-Tropsch process (Chang, 1983). Methanol is efficiently converted into olefins and aromatic compounds, but the reaction chemistry is more complex than this simple equation suggests. Chemical equations for each aspect of the process should be developed for accuracy and economics.

The methanol feed, vaporised by heat exchange with reactor effluent gases, is converted to an equilibrium mixture of methanol, dimethyl ether (DME), and water in a first-stage reactor containing an alumina catalyst in the process (which can use a fixed bed reactor or a fluid bed reactor). This is combined with recycled light gas, which serves to remove reaction heat from the highly exothermic MTG reaction, and enters the reactors containing zeolite catalyst, where reaction temperature conditions are 360–415°C at a pressure of approximately 300–350 psi. Because the MTG process produces primarily gasoline, a variant of that process that produces both gasoline and distillate fuel has been developed. The combined process (MTO and MOGO) generates gasoline and distillate in various proportions and, if necessary, can be stopped at a point to generate olefin by-products. Methanol is converted over a zeolite catalyst to produce high yields of olefins with some ethylene and low-boiling light saturated hydrocarbons in the MTO process.

Catalyst and process variables that increase methanol conversion generally reduce olefins yield. Typical conversion rates in the MTO process exceed 99.9%. The coked catalyst is removed from the reactor on a continuous basis and burned in a regenerator. Using a zeolite catalyst, low-molecular-weight olefins are converted into oligomers in the gasoline-boiling range via the MOGD process. Other distillate products are made as well. The ratio of gasoline to distillate product can range from 0.2 to >100 depending on process conditions.

Direct conversion of natural gas (methane) to liquid fuels entails converting methane to the desired liquid fuels without using syngas. Extensive research has been conducted on direct upgrading routes such as direct partial oxidation to oxygenates, oxidative coupling to higher hydrocarbons, and pyrolysis to higher hydrocarbons. The Rentech process, as described in a series of patents, takes advantage of the synergy between iron-based Fischer-Tropsch synthesis and plasma-based syngas production.

Plasma-based syngas production, for example, is a front-end conversion process in which hydrocarbon feedstock, such as natural gas, is fed to a high- or low-temperature plasma torch or electrical arc reactor. The arc converts the feedstock into a syngas of hydrogen and carbon monoxide. The Fischer-Tropsch process can then convert this syngas into liquid hydrocarbons. A portion of the syngas is converted to carbon dioxide during Fischer-Tropsch synthesis using iron-based catalysts. Tail gas is recycled by returning the carbon dioxide extracted from the process to the plasma torch, where it is efficiently converted into carbon monoxide, which is then fed into the Fischer-Tropsch reactor.

The plasma can reform natural gas using only carbon dioxide from the Fischer-Tropsch reactor, producing syngas almost entirely of carbon monoxide and hydrogen. The reactor tail gas components, in addition to the carbon dioxide produced in the Fischer-Tropsch reactor, can be converted into additional carbon monoxide and hydrogen for the Fischer-Tropsch reactor feedstock. This synergy between iron-based Fischer-Tropsch synthesis and plasma-based syngas production significantly improves carbon conversion efficiency and is an excellent technique for reducing carbon dioxide emissions while producing sulfur- and aromatic-free fuels. Furthermore, plasma-based syngas production has significant advantages over other methods of producing syngas because it does not require an air separation plant and has virtually no moving parts. Oxygen-permeable membranes have the potential to replace expensive cryogenic oxygen plants in the production of oxygen. The membrane can be used to convert natural gas to synthesis gas via a partial oxidation reaction when combined with an appropriate catalyst on the oxygen-lean side.

$$2CH_4 + O_2 \rightarrow CO + 2H_2$$

Fischer-Tropsch diesel has a high cetane number and can be produced without aromatics or sulphur. It can be used in traditional distribution infrastructure and diesel engines, and it emits less nitrogen oxide and particulate matter than petroleum diesel. The Fischer-Tropsch diesel's near-zero sulphur content may also enable exhaust aftertreatment, resulting in any further emission reductions. As a result, this diesel could help displace the diesel fuel commonly used to power medium- and heavy-duty vehicles while also meeting specifications for extremely low-sulfur diesel fuel. Fischer-Tropsch diesel, if approved, could be designated as an alternative fuel as early as winter 2004. The previously described syngas production routes are based on proven technologies and provide us with reliable origins for the development of processes that have the potential to further reduce both capital and operating costs.

Straight catalytic autothermal reforming can be advantageous for some syntheses. Lurgi has used this process to produce methanol as well as treat Fischer-Tropsch tail gases. Whereas the hot hydrogen-rich primary reformer effluent in a secondary reformer configuration is self-igniting, ignition of a straight autothermal reformer requires the use of a noble-metal-promoted combustion catalyst. To eliminate the possibility of backburning, the velocity in the ignition-catalyst area must be kept high.

These high velocities cause mechanical attrition of the expensive ignition catalyst over time. The process arrangement has been modified as part of the ongoing development of its reforming processes to bring the operating conditions closer to that of a secondary reformer, thus eliminating the need for the ignition catalyst. The HCT reforming technology employs the so-called HCT reformer tube. In principle, this is a standard sicp reformer tube, catalyst-filled, heated from the outside, and normally designed for process gas downflow through the catalyst bed. On the inside, however, it contains a double helix made of tubes of appropriate material embedded in the catalyst. The reformed process gas flows through this double helix in the opposite direction of the procedure gas flow through the catalyst bed, transferring some of its sensible heat to the reforming process. Based on calculations and practical experience, this intrinsic heat transfer covers up to 20% of the process gas's sensible and reaction heat at an inlet temperature of 450°C and a reaction-end temperature of 860°C. In addition to the fuel savings, an investment savings of about 15% can be expected, the majority of which is due to the smaller convection bank required.

Resids

Arab scientists developed methods for distilling petroleum approximately 2000 years ago, and interest in the thermal product of petroleum (nafta; naphtha) was piqued when it was discovered that this material could be used as an illuminant and as a supplement to asphalt incendiaries in warfare. The discovery also resulted in the creation of resids, which could have been used if the supply of bitumen or natural asphalt from natural seepages became limited. A residuum (plural residua, also shortened to resid, plural resids) is the residue left over after nondestructive distillation has removed all volatile materials from petroleum. The distillation temperature is typically kept below the temperature at which the rate of thermal decomposition of petroleum constituents is minimal.

Residua are black, viscous materials produced by distilling crude oil at atmospheric pressure (atmospheric residuum) in an atmospheric distillation unit (atmospheric tower, atmospheric pipe still) or at reduced pressure (vacuum residuum) in a vacuum distillation unit (vacuum tower, vacuum pipe still). Depending on the nature of the petroleum from which the residua was obtained or the cut point of the distillation, they may be liquid at room temperature (generally, atmospheric residua) or almost solid (generally, vacuum residua). Asphaltenes are molecular polar species with very high molecular weight that are soluble in carbon disulfide, pyridine, aromatic hydrocarbons, and chlorinated hydrocarbons. They are the petroleum nonvolatile fractions that are separated from the atmospheric distillation unit to form the vacuum distillation unit (Figure 9.2).

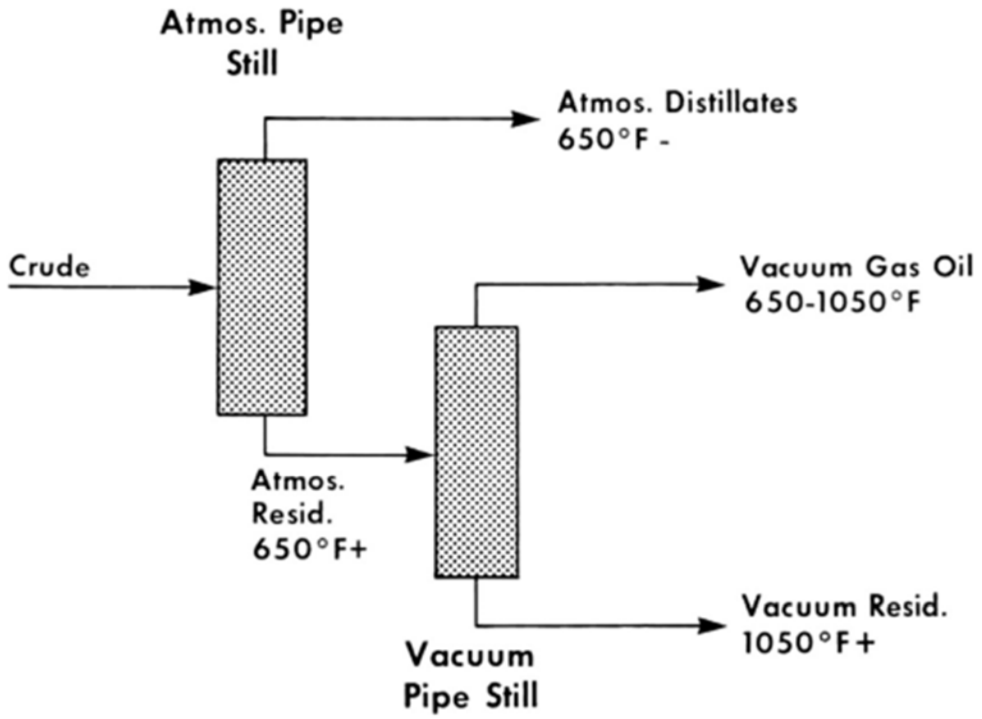

Figure 9.2 Represent the resid production.

When a residuum is extracted from crude oil and hydrothermal method has begun, it is more commonly referred to as pitch. The differences between parent petroleum and residua are caused by the relative amounts of various constituents present, which are removed or remain due to their volatility. The chemical composition of an asphaltic crude oil residuum is complex and dependent on the method of production (i.e., the temperature at which the distillation is performed). Physical fractionation methods typically yield high proportions of asphaltenes and resins, even up to 50% (or higher) of the residuum. Furthermore, the presence of ash-forming metallic constituents, such as vanadium and nickel organometallic compounds, is a distinguishing feature of residua and heavy oils. Furthermore, the greater the concentration of sulphur and metals in the residuum and the greater the deterioration in physical properties, the deeper the cut into the crude oil. Despite the fact that a resid is a manufactured product, the constituents occur naturally as part of the native petroleum, assuming that no thermal decomposition occurred during distillation. Residua are produced specifically during petroleum refining, and the properties of the numerous residua are determined by the cut point or boiling point at which distillation is terminated.

Resid Production

The process of producing a nonvolatile residue entails diluting everything possible from crude petroleum. This is typically accomplished in stages, with atmospheric pressure distillation removing the lower-boiling fractions and yielding an atmospheric residuum (reduced crude) that may contain higher-boiling (lubricating) oils, wax, and asphalt. Metal trays or plates divide the atmospheric distillation tower into horizontal sections, each of which is equivalent to a still. The more trays there are, the more redistillation there is, and thus the better the fractionation or separation of the mixture fed into the tower. A crude petroleum fractionation tower may be 13 feet in diameter and 85 feet tall, with 16 to 28 trays. The feed to a typical tower passes through the vaporising or flash zone, which is devoid of trays. The vast majority of trays are usually found above this area. Depending on the type of feedstock and the desired characteristics in the products, the feed to a bubble tower can be at any point from top to bottom, with trays above and below the entry point.

However, the typical permissible temperature in the vaporising zone to which the feedstock can be subjected is 350°C (660°F). Above this temperature, the rate of thermal decomposition accelerates significantly; if decomposition occurs within a distillation unit, it can result in coke deposition in the heater pipes or in the tower itself, resulting in unit failure. Some distillation units use vaporising zone temperatures of up to 393°C (740°F) to reduce residence time in the hot zone. When using a higher temperature, use caution because units that are unable to maintain the specified petroleum flow-through can suffer from residue decomposition (due to longer residence times in the vaporising zone) and poorer-quality asphalt.

The oils (and wax) are removed as overhead products during vacuum distillation of the reduced crude, while the asphalt remains as a bottom (or residual) product. The majority of the nonvolatile polar functionalities and high-molecular-weight species in the original crude oil are concentrated in the vacuum residuum (Speight, 2000), conferring desirable or undesirable properties on the asphalt. At this point, the residuum is commonly and incorrectly referred to as pitch, and it has a softening point that is proportional to the amount of oil removed and increases with increasing overhead removal. The pour point is elevated in tandem with the softening point: the more oil distilled from the residue, the higher the softening point. Because the boiling point of the heaviest cut obtained by distillation at atmospheric pressure is limited by the temperature in the vaporising zone, unless cracking distillation is preferred, vacuum distillation has seen widespread use in petroleum refining. When the feedstock is needed for the production of lubricating oils, further fractionation without cracking is desired, which can be accomplished through vacuum distillation.

Vacuum distillation of reduced crude yields the following fractions:

1. Heavy gas oil, an overhead product used as a catalytic cracking stock or, after appropriate treatment, as a light lubricating oil

2. Lubricating oil obtained as a byproduct (typically three fractions: light, intermediate, and heavy).

3. Vacuum the residuum, a nonvolatile product that can be used directly as asphalt or as a precursor to asphalt.

The residue can also be used as a feedstock in a coking operation or blended with gas oils to make heavy fuel oil.

CHAPTER 10

ASPHALTENE SEPARATION

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The asphaltene fraction is defined as the portion of the feedstock precipitated when a large excess (40 volumes) of a low-boiling liquid hydrocarbon (such as n-pentane or n-heptane) is added to 1 volume of crude oil . The preferred hydrocarbon is n-heptane, though n-pentane is still used (Speight et is the most complex fraction in petroleum and has the highest molecular weight. The asphaltenes content indicates how much coke can be expected during processing. The residues are mixed with a slight excess (usually >30 volumes hydrocarbon per volume of sample) of a low-boiling hydrocarbon such as n-pentane or n-heptane in any of the methods for determining the asphaltene content. To compensate for the presence of the solvent, a solvent such as toluene may be used prior to the addition of the low-boiling hydrocarbon, but an additional amount of the hydrocarbon (usually >30 volumes hydrocarbon per volume of solvent) must be added. The insoluble material (the asphaltene fraction) is separated (by filtration) and dried after a predetermined time. The yield is expressed as a percentage of the original sample

It should be noted that in any of these tests, different hydrocarbons (such as n-pentane or n-heptane) will yield different asphaltene fraction yields, and if the presence of the solvent is not compensated for by the use of additional hydrocarbon, the yield will be incorrect. Furthermore, if the hydrocarbon is not present in large quantities, the yields of the asphaltene fraction will vary and be incorrect. The precipitation number is frequently equated with the asphaltene content, but there are several obvious problems with this. For example, the precipitation number method (ASTM D-91) recommends using naphtha with black oil or lubricating oil, and the precipitating number is the amount of insoluble material (as a% v/v of the sample). In the test, 10 ml of sample is mixed with 90 ml of ASTM precipitation naphtha (which may or may not have a constant chemical composition) in a graduated centrifuge cylinder and centrifuged at 600 to 700 rpm for 10 minutes. The amount of material on the bottom of the centrifuge cone is measured until repeat centrifugation yields a value within 0.1 ml (the precipitation number). Obviously, this can vary greatly depending on the asphaltene content.

Another test method (ASTM D-4055) can be used to determine pentane insoluble materials larger than 0.8 m in size. A sample of oil is mixed with pentane in a volumetric flask, and the oil solution is filtered through a 0.8-mmembrane filter, which is then washed with pentane to completely transfer the particulates onto the filter, which is then dried and weighed to give the yield of pentane-insoluble materials.

Fractionation of Deasphaltened Oil

After the asphaltene fraction is removed, further fractionation of residues is possible by varying the hydrocarbon solvent.

However, most resid composition analyses have relied on fractional separation. The separation methods used divide the residue into operationally defined fractions. Three types of resid separation procedures are now in use: (1) chemical precipitation, in which n-pentane separation of asphaltenes is followed by chemical precipitation of other fractions with increasing concentrations of sulfuric acid (ASTM D-2006); (2) adsorption chromatography using a clay-gel procedure, in which the remaining constituents are separated by selective adsorption or desorption on an adsorbent after removal of the asphaltenes (ASTM D- (ASTM D-3593).

These schemes' fractions are defined operationally or procedurally. The solvent used to precipitate them, for example, determines the amount and type of asphaltenes in a solution. A resid's chemical components are not well defined after fractional separation. Only the materials separated should be defined in terms of the specific test procedure. However, thermal degradation fractions are not considered to be naturally occurring constituents of resid. To determine the amount of carbenes and carboids in resid, use the test method for determining the toluene-insoluble constituents of tar and pitch.

Many studies of the relationships between composition and properties consider only the concentration of asphaltenes, regardless of any quality criterion. However, there is a distinction to be made between asphaltenes found in straight-run residua and those found in broken residua. Because asphaltenes are a solubility class rather than a distinct chemical class, the composition of this fraction varies greatly when produced by different processes. For example, liquefied gases such as propane and butane can precipitate up to 50% of the residue by weight. In contrast to pentane-precipitated asphaltenes, which are typically brown, amorphous solids, the precipitate is a black, tacky, semisolid material. The insoluble, brown, amorphous asphaltenes and soluble, near-black, semisolid resins produced by treating the propane precipitate with pentane are, as far as can be determined, equivalent to the polymers isolated by adsorption techniques.

Adsorption chromatography separation begins with the preparation of a porous bed of finely divided solid, the adsorbent. The adsorbent is typically housed in an open tube (column chromatography); the sample is introduced at one end of the adsorbent bed and induced to flow through the bed using a suitable solvent. The various components are held (adsorbed) to varying degrees as the sample moves through the bed, depending on the chemical nature of the component. Thus, molecules that are strongly adsorbed spend a significant amount of time on the adsorbent surface rather than in the moving (solvent) phase, whereas components that are only slightly adsorbed move through the bed relatively quickly.

Three ASTM methods are available for separating a feedstock into four or five constituent fractions (Speight, 2001, and references cited therein). It is worth noting that as methods have evolved, the use of pentane (ASTM D-2006 and D-2007) has given way to heptane (ASTM D-4124) for asphaltene separation. This is consistent with the production of a more consistent fraction that represents petroleum's higher-molecular-weight complex constituents. Two of the methods (ASTM D-2007 and D-4124) recommend using adsorbents to fractionate the deasphaltened oil, but the third (ASTM D-2006) recommends using various grades of sulfuric acid to separate the substance into compound types. Caution is advised when using this method because it does not work well with all feedstocks. Complex emulsions can be produced, for example, when the sulfuric acid method (ASTM D-2006) is used to separate heavy feedstocks.

Standard resid analyses, such as elemental composition and molecular weight determinations, have not proven to be reliable predictors of processability, and determining average structural features does not appear to be very helpful. The results of any of the evaluation techniques described here provide an indication of resident behaviour. The data can also be used to provide the refiner with an understanding of the differences between different residua, indicating how the resids should be processed, as well as to predict product properties.

Because of the complexities of residences, relying solely on bulk properties to predict behaviour has drawbacks. As a result, it appears that fractionating resids into components of interest and studying the components is a better approach than obtaining data on whole residua. It may be possible to obtain a detailed overview of feedstock composition that can be used for process predictions by carefully selecting a characterization scheme. In refinery operations, the use of composition data to model resid behaviour during refining is becoming increasingly important. Resids can be thought of as composites of four major operational fractions, which allows different resids to be compared on a relative basis to provide a very simple but convenient feedstock map However, such a map provides no indication of the complex interrelationships of the various fractions, though such data can be used to predict feedstock behaviour. To obtain a more representative indication of petroleum composition, the composition studies must be taken a step further by subfractionation of the major fractions. Long and Speightexpanded on this concept by creating a different type of compositional map that used the molecular weight distribution and the molecular-type distribution as coordinates. The fractions were characterised by a solubility parameter as a measure of the polarity of the molecular types, and the separation used an adsorbent such as clay. Gel permeation chromatography can be used to determine the molecular weight distribution (Figure 10.1).

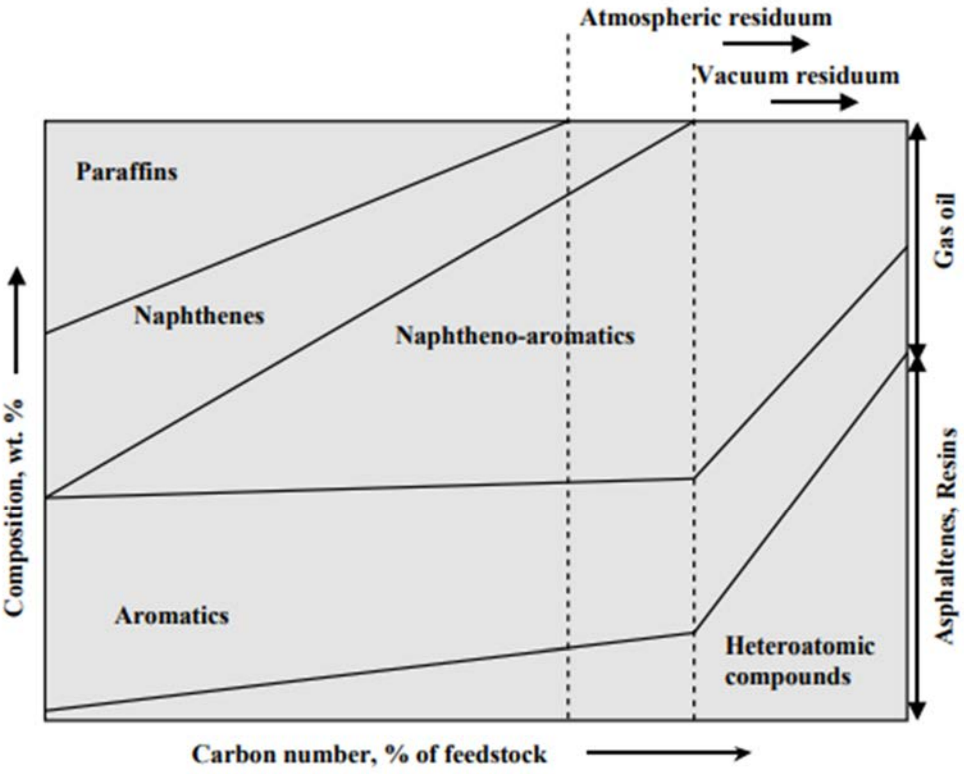

Figure 10.1 Represent the Simplified representation and resid composition.

Resid Conversion

Residual quality is an important consideration in the selection and efficiency of conversion technology. Metal levels (vanadium and nickel) are a well-known feature of many residences. The Conradson carbon and hydrocarbons content of residences is also high, posing challenges to upgrading technology**.**

Visbreaking

Visbreaking is a poor heat process that was originally used to reduce residual viscosity in heavy fuel oil applications. The visbreaking process currently converts resids (15-20% v/v conversion) to some liquid fuel boiling range liquids, with visbroken resid being used to meet heavy fuel oil specifications. Because the process is not intended to produce coke formation, it operates with the induction period prior to carbon deposition. A visbreaker reactor is similar to a delayed coker in that it consists of a furnace tube followed by a soaker drum. The drum, on the other hand, is much smaller in volume in order to limit the residence time, with the entire liquid product flowing overhead. The entire visbreaker could also be a long tube coiled within a furnace. Differences in resid qualities can cause coke to form in the vessel, necessitating the use of coke removal protocols.

Visbreaking can be used on atmospheric residues, vacuum residues, and solvent deasphalter bottoms (asphalt). Visbreaking the atmospheric residue in conjunction with a thermal cracker was a common operation to reduce fuel oil while producing additional light distillates. When looking for feedstock for fluid catalytic cracking, visbreaking is typically applied to vacuum residues and is frequently used as a mild vacuum residue conversion process. Lower-boiling distillates are recovered for use as transportation fuels, while higher-boiling distillates are recovered for use as feedstock for the fluid catalytic cracking unit. A high-temperature coil visbreaker enables the recovery of a high-boiling distillate from the fractionator. A separate vacuum flasher is typically required for lower-boiling distillates and soaking drum technology. The requirement to produce a stable fuel oil limits conversion in a visbreaker. As the resin is thermally cracked, reactions occur that increase the asphaltene content, which, combined with the reduction (by thermal decomposition) of the resins holding the asphaltene constituents in solution, causes the asphaltenes to precipitate.

Coking

Coking is a high-temperature (450-500°C [842-932°F]) process that is the most commonly used conversion method for resids with a high content of polynuclear aromatic systems (low hydrogen, high heteroatoms, high Conradson carbon). Coking converts polynuclear aromatic systems to coke (a low-value product) and overhead (high-value distillates), which can then be upgraded to liquid fuels and other products. Delayed coking is the most traditional and widely used method of converting residences. The resid is heated in a furnace via a long tube and then reacted via flow into the bottom of a high, cylinder, insulated drum. The drums are used in pairs, one onstream and one downstream. The volatile (overhead) products are routed to a fractionator, while coke accumulates in the drum. High-boiling liquid products can be recycled to the furnace and recirculated through the coke drum. When the drum is full of coke, the hot feed is turned off and the second drum is turned on. The coke is removed from the offstream drum using high-pressure water, and the onstream-offstream cycle (typically 16 hours) is reversed. Resid conversion also makes use of the fluid coking and flexicoking processes.

The hot residue is sprayed on a hot, fluidized bed of coke particles in a reactor during the fluid coking process. The volatile products (overhead) are transferred to a fractionator, while the coke particles are removed from the reactor's bottom and transferred to another vessel, the burner or regenerator. The excess coke is partially burned with air to provide heat for the process before being recirculated back to the reactor. A third vessel (the gasifier) is added to the fluid coking flow in the flexicoking process, which is very similar to the fluid coking process. Excess coke is gasified with steam and air to create a low-Btu gas containing hydrogen, carbon monoxide, nitrogen, and hydrogen sulphide. After the hydrogen sulphide has been removed, the low-Btu gas is burned as a clean fuel inside the refinery or in a nearby power plant.

Resid Catalytic Cracking

Resid catalytic cracking has much better selectivity to desired products (high-gasoline and low-gas yields) than for coking or hydroconversion. In fluid catalytic cracking, feed is sprayed on zeolite catalyst in a short-contacttime riser reactor. The vaporized product flows to a fractionator while the catalyst with coke and adsorbed hydrocarbons flows to a fluidized bed regenerator in which the coke and hydrocarbons are burned off the catalyst. Fluid catalytic cracking requires much more higher-quality feeds than coking or hydroconversion. This is because of expensive zeolite catalysts, intolerance to sodium, nickel, vanadium, and basic nitrogen, as well as limitations on the amount of coke that can be burned in the regeneration step by cooling capacity. As a result, the feed in resid catalytic cracking is at worst an excellent-quality atmospheric resid, but mixtures of vacuum gas oil and atmospheric resids are more common. The total feed is limited to Conradson Carbon Residues of 3 to 8 wt%, depending on the cooling capacity.

Hydroconversion

Hydroconversion is the combination of thermal cracking and hydrogenation. The addition of hydrogen lengthens the coke induction period by lowering the solubility parameter by hydrogenating polynuclear aromatic systems, but primarily by preventing free radicals from combining to form larger polynuclear aromatic systems. As a result, hydroconversion of vacuum residues to volatile liquids can exceed 85%, compared to 50-60% for coking. However, there are costs associated with hydrogen and catalyst, high-pressure vessels, catalyst poisoning, the difficulty of diffusing asphaltenes through small pores, and intolerance to coke and sediment formation. Because the high level of sulphur in resid feeds will poison other hydrogenation catalysts, the active catalyst must be a transition metal sulphide.

Desulfurization units, both atmospheric and vacuum, are commonly used to desulfurize residue as a preparatory measure for feeding low-sulfur vacuum gas-oil feed to cracking units (fluid catalytic cracking units and hydrocracking units), low-sulfur residue feed to delayed coker units, and low-sulfur fuel oil to power plants. For direct catalytic hydroprocessing of residue, two types of processing elements are used. These are either (1) down-flow, trickle phase reactor systems (fixed catalyst bed) or (2) liquid recycle and back mixing systems.

Fixed Bed Units

Because metal removal is one of the quickest reactions, and because metals accumulate in the pores of electrocatalysts, a guard bed is commonly used in front of the fixed bed. When there is insufficient metal removal in the guard bed, the feed is switched to a second guard room with fresh catalyst, and the catalyst in the first guard bed is replaced. As a result, the fixed bed is shielded from metal deposition. To hydrogenate the resid's largest macromolecules, the asphaltenes, some or all of the catalysts must have pores 50-100 m in diameter. Even with these precautions, it is difficult to achieve run lengths of more than one year on fixed bed hydroconversion units with low pressure resid feeds and 50% or higher conversions to volatile liquids. This is due to coke deactivation of the catalyst or coke and soil particles formation downstream of the reactor.

Solvent Deasphalting

Though not strictly a conversion process, solvent deasphalting is a separation process that represents another step in the reduction of residue production. The process takes advantage of the fact that maltenes are more soluble than asphaltenes in light paraffinic solvents. This solubility rises with increasing solvent molecular weight and falls with temperature increases. There are limitations to how deep a solvent deasphalting unit can cut into in the residue or how much deasphalted oil can be produced, as with vacuum distillation. In the case of solvent deasphalting, these constraints are typically: (1) the quality of deasphalted oil required by conversion units, and (2) the stability and quality of residual fuel oil.

The flexibility of solvent deasphalting allows it to meet a wide range of deasphalted oil quality. The process rejects asphaltene constituents and metal constituents very well, with varying selectivity (depending on the feedstock) for other coke precursors, but less selectivity for sulphur constituents and nitrogen constituents. The process has the disadvantages of performing no conversion, producing a very high-viscosity by-product pitch, and where high-quality deasphalted oil is required, the solvent deasphalting process is limited in the quality of feedstock that can be economically processed. The solvent deasphalting process's viability is determined by the potential for upgrading the deasphalted oil as well as the difference between the value of the cutter stocks and the price of elevated residual fuel oil. If there is an asphalt outlet (from the unit) and the transformation capacity to upgrade the deasphalted oil, solvent deasphalting can be a very appealing option for residential conversion.

Liquid Fuels from Oil Sand

Liquid fuels are made from a variety of sources, most common of which is petroleum. 6Other sources of liquid fuels, however, include oil sand (Berkowitz and Speight, 1975; Speight, 1990, and references cited therein) and coal. Coal can also be used as a source of liquid fuels to a lesser extent (Speight, 1994, and references cited therein). When liquid fuels are produced from a source including such oil sand, the initial product is often referred to as synthetic crude oil or syncrude, which is a liquid fuel that does not occur naturally in the present context.

Oil sand (also known as tar sand and asphalt sand) is a sand deposit that has been impregnated with bitumen, an organic material. Natural asphalt is another name for the organic material that soaks up various sand deposits; however, it is less precise than bitumen. The terms oil sand and tar sand are scientifically incorrect because oil sand does not contain oil and tar is most commonly produced from bituminous coal, in addition to being widely understood to refer to a product derived from coal, though it is preferable to specify coal tar if there is any possibility of ambiguity. Thus, oil sand should technically be called coal sand because the hydrocarbonaceous material is bitumen (soluble in carbon disulfide) rather than oil. The term "oil sand" refers to the synthetic crude oil that can be produced from bitumen.

Oil sand is a mixture of sand, water, and bitumen, with the sand component being predominantly quartz in the form of rounded or subangular particles, each of which is wet with a film of water (as far as is known for the Athabasca deposit). A bitumen film surrounds the wetted sand grains, filling in the gaps between them. The remaining void volume is filled with connate water and, on occasion, a small volume of gas. High-grade oil sand contains about 18% bitumen by weight, which may have the same consistency (viscosity) as an atmospheric or vacuum petroleum residuum.

Bitumen has been defined very loosely and arbitrarily based on API gravity or viscosity; it is quite arbitrary and far too broad to be technologically accurate. Attempts to rationalise the definition based on viscosity, API gravity, and density have been made, but they suffer from a lack of technical accuracy. For example, the commonly used line of demarcation between oil sand bitumen and heavy oil is 10° API. However, one must question whether the distinction between 9.9° API gravity oil and 10.1° API oil is truly significant. Both measurements are within standard laboratory test method margins of error. Similarly, the use of viscosity data is called into question because the difference between oil with a viscosity of 9,950 cp and oil with a viscosity of 10,050 cp is minimal, and both measurements are within the margins of error for standard laboratory test methods.

Oil sand bitumen in oil sand deposits is a highly viscous hydrocarbonaceous material that cannot be recovered in its natural state through a well using conventional oil well production methods, including currently used enhanced recovery techniques, as specified in US government regulations. As a result, it is not surprising that the properties of bitumen extracted from oil sand deposits differ significantly from those of conventional crude oil (recoverable via primary and secondary methods) and heavy oil (recoverable by enhanced oil recovery techniques). Chemically, the material should be referred to as bituminous sand rather than oil sand because the organic matrix is bitumen, a hydrocarbonaceous material composed primarily of carbon and hydrogen, with trace amounts of nitrogen, oxygen, sulphur, and metals (especially nickel and vanadium.

Current commercial bitumen recovery operations in oil sand formations employ a mining technique. Following this, bitumen is upgraded and refined to produce synthetic crude oil. Other methods for recovering bitumen from oil sand include mining, followed by additional processing, or operating on the oil sands in situ. Depending on the deposit, the API gravity of oil sand bitumen ranges from 5° API to approximately 10° API; viscosity is very greater, and volatility is low. Bitumen has a high viscosity, ranging from several thousand to one million centipoises, with higher viscosities recorded. Bitumen volatility is low, and only trace amounts of naphtha and kerosene are present. The lack of mobility of bitumen necessitates a mining step followed by the hot water process, which is the only commercially successful method of recovering bitumen from mined oil sand to date. Many process options have been tested with varying degrees of success, and one of these options may eventually replace the hot water process. Furthermore, bitumen is relatively deficient in hydrogen, necessitating significant hydrogen addition during refining. At the moment, bitumen is commercially upgraded through a combination of carbon rejection (coking) and product hydrotreating.

Coking, the preferred process for residua, is also the preferred process for bitumen conversion. Bitumen is currently commercially converted using delayed coking and fluid coking. Bitumen is converted into distillate oils, coke, and light gases in each case. Coker distillate is a partially upgraded material that can be used as a feed for hydrodesulfurization to produce low-sulfur synthetic crude oil. The potential for producing liquid fuels from oil sand is high in the coming decades, and the liquid fuels produced from these deposits offer a means of alleviating shortfalls in the supply of liquid fuels. The only commercial operations for bitumen recovery and upgrading take place in northeast Alberta, Canada, near Fort McMurray, where bitumen from the Athabasca deposit is converted to synthetic crude oil. As a result, studies of these Canadian deposits provide the majority of the data available for bitumen inspection and behaviour determination. Other sources of bitumen work is fragmented and spasmodic. The exception is bitumen from Utah deposits, where ongoing programmes have been in place for more than three decades at the University of Utah.

Occurrence And Reserves

The occurrence and reserves of oil sand bitumen that are available for production of liquid fuels are known to an approximation, but the definitions by which these reserves are estimated need careful consideration. Best estimates are all that are available. Thus, the world reserves of conventional petroleum (arbitrarily defined as having a gravity equal to or greater than 20° API) are reported to be composed of approximately 1,195 billion barrels (1,195 × 109 bbl) or 30% by volume of the total reserves (of petroleum plus heavy oil plus bitumen). Heavy oil (arbitrarily defined as having a gravity greater than 10° API but less than 20° API) is reported to be 690 billion barrels (690 × 109 bbl) or 15% by volume of the total reserves. Oil sand bitumen (arbitrarily defined as having a gravity equal to or less than 10° API) is reported to be 1,920 billion barrels (1,920 × 109 bbl) or 55% by volume of the total reserves. However, the bitumen reserves contain extra heavy oil, which term is sometimes used to describe bitumen.

The API gravity of this material is less than 10° API, but the viscosity may fall into a different range when compared to bitumen viscosity. And in such reserves estimations, there is often no mention of the method of recovery on which the definition of oil sand bitumen hinges. Therefore, estimations of bitumen availability must be placed in the correct definitional context and, more particularly, in the context of the available recovery method. Oil sand deposits are widely distributed throughout the world in a variety of countries, and the various deposits have been described as belonging to two types:

Although gradations between deposit types are unavoidable (Walters, 1974; Phizackerley and Scott, 1978; Meyer and Dietzman, 1981), there are two types of traps: (1) stratigraphic traps and (2) structural traps. The majority of the work on specific geological and geochemical aspects of the formation has, once again, been done on the Athabasca deposit. As a result, the emphasis of this chapter is on the work done on the Canadian oil sand deposits.

The largest oil sand deposits in Canada are in Alberta and Venezuela, with smaller deposits in the United States (mostly in Utah), Peru, Trinidad, Madagascar, the former Soviet Union, the Balkan states, and the Philippines. Oil sand deposits are larger in northwestern China (Xinjiang Autonomous Region); at some locations, bitumen appears on the land surface around Karamay.

The Athabasca deposit, along with the nearby Wabasca, Peace River, and Cold Lake deposits, is estimated to contain approximately 2 trillion barrels (2 1012 bbl) of bitumen in Canada. Venezuelan deposits may contain at least one trillion barrels (1.0 1012 bbl) of bitumen. Oil sand deposits containing approximately 20 million barrels (20 106 bbl) of bitumen have also been discovered in the United States, Albania, Italy, Madagascar, Peru, Romania, Trinidad, Zaire, and the former USSR. The oil sand deposits in the United States are divided into several separate deposits in various states but because many of these deposits are small, information on most of them is limited.

The deposits of California are concentrated along the coast west of the San Andreas Fault. The Edna deposit, located halfway between Los Angeles and San Francisco, is the largest. The deposit occurs as a stratigraphic trap, covers approximately 7000 acres, and extends from outcrop to a depth of 100 feet (30 metres). The Sisquoc deposit (Upper Pliocene) is the second largest in California, with a total thickness of about 185 feet (56 metres), occurring over an area of about 175 acres and an overburden thickness ranging from 15 to 70 feet (4.6 and 21 m).

Santa Cruz, California's third deposit, is about 56 miles (90 kilometres) from San Francisco. Asphalt, DavisDismal Creek, and Kyrock are the Kentucky oil sand deposits. The Triassic Santa Rosa sandstone contains oil sand deposits in New Mexico. Finally, the oil sand deposits in Missouri cover an area of about 2000 mi2, and the individual bitumen-bearing sands are about 50 ft (15 m) thick, except where they occur in channels that can be up to 250 ft (76 m) thick. Venezuelan oil sand deposits are found in the Officina/Tremblador tar belt, which is thought to contain bitumen-impregnated sands to a similar extent as Alberta, Canada. Bitumen with an API gravity less than 10° is the organic material. The Bemolanga (Madagascar) deposit is the world's third largest oil sand deposit, spanning 150 square miles in western Madagascar and containing overburden ranging from 0 to 100 feet (0 to 30 m). The average pay zone thickness is 100 feet (30 metres), and the total bitumen in-place is estimated to be 2 billion barrels (approximately 2 109 bbl). Selenizza, Albania, has Europe's largest oil sand deposit. This region also contains the Patos oil field, which has extensive bitumen impregnation.

The Trinidad Asphalt Lake (located on the Gulf of Paria, 12 miles west-southwest of San Fernando and above sea level) is carved out of Miocene sheet sandstone. The Romanian deposits are found at Derna, in a triangular section east and northeast of Oradia between the Sebos Koros and Berrettyo rivers (along with Tataros and other deposits). Oil sands are found in Cheildag, Kobystan, and on the south flank of the Cheildag anticline; approximately 24 million barrels (24 106 bbl) of bitumen are present. Other deposits in the former USSR can be found in the Olenek anticline (northeast of Siberia), and it has been claimed that the extent of bitumen impregnation in Permian sandstone is on the same order of magnitude (in area and volume) as the Athabasca deposits. Oil sands have also been discovered in Subovka sands, and the Notanebi deposit (Miocene sandstone) is said to contain 20% bitumen by weight. The Kazakhstan presence, near the ShubarKuduk oil field, on the other hand, is a bituminous lake with a bitumen content estimated to be in the order of 95% by weight of the deposit.

There are oil sand deposits in the southern Llanos of Colombia, Burgan in Kuwait, and the Inciarte and Bolivar coastal fields of the Maracaibo Basin, but little is known about them. There are also small deposits in the Philippines' Leyte Islands, Thailand's Mefang Basin, Chumpi, and near Lima (Peru). Oil sand deposits have also been discovered in Spain, Portugal, Cuba, Argentina, Thailand, and Senegal, but the majority are poorly defined and are estimated to contain less than 1 million barrels (1 106 bbl) of bitumen (in-place). The fact that commercialization has occurred in Canada does not imply that commercialization of other oil sand deposits is imminent. There are significant differences between Canadian deposits and deposits in the United States and the rest of the world that may preclude applying the principles applied to Canadian oil sand deposits to other oil sand deposits.

CHAPTER 11

CLASSIFICATION OF BITUMEN

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The sulphur content, carbon residue, nutrient content, and metals content of bitumen can all be measured. API gravity and viscosity, for example, assist the refinery operator in understanding the nature of the material to be processed. Products derived from high-sulfur feedstocks frequently necessitate extensive treatment to remove (or alter) the corrosive sulphur compounds. Nitrogen compounds and various metals found in crude oils will significantly reduce catalyst life. The carbon residue shows the quantity of thermal coke that may be formed at the expense of the liquid products.

Chemical Composition

The sulphur content, carbon residue, nutrient content, and metals content of bitumen can all be measured. API gravity and viscosity, for example, assist the refinery operator in understanding the nature of the material to be processed. Products derived from high-sulfur feedstocks frequently necessitate extensive treatment to remove (or alter) the corrosive sulphur compounds. Nitrogen compounds and various metals found in crude oils will significantly reduce catalyst life. The carbon residue shows the quantity of thermal coke that may be formed at the expense of the liquid products.

Bitumen Recovery

Current commercial operations involve mining oil sand, transporting it to a processing plant, extracting the bitumen, and disposing of the waste sand. The only commercial oil sand mining operation is located in Canada's Athabasca deposit. Suncor's processing and mining plant, located 20 miles north of Fort McMurray, Alberta, began operations in 1967. The Syncrude Canada mining and processing plant, located 5 miles (8 kilometres) from the Suncor plant, began operations in 1978. In both projects, muskeg, an organic soil similar to peat moss that ranges in depth from a few inches to 23 ft (7 m), covers roughly half of the terrain. However, the majority of the overburden is Pleistocene glacial drift and Clearwater Formation sand and shale. The total overburden thickness ranges from 23 to 130 feet (7 to 40 metres). The underlying oil sand strata average about 150 feet (45 metres), but typically 16 to 33 feet (5 to 10 metres) must be discarded due to bitumen content less than the economic cut-off grade designated by either plant, which is typically on the order of 5% by weight.

Suncor and Syncrude both expect to produce 500,000 barrels per day of synthetic crude oil (mostly in the liquid fuel boiling range) over the next 5 to 10 years. There are two approaches to open-pit oil sand mining. The first employs a few custom-designed mining units, such as bucket-wheel excavators and large draglines, in conjunction with belt conveyors. In the second approach, a variety of smaller mining units of conventional design, such as scrapers and truck-and-shovel operations, are used. Each method has advantages and disadvantages. Suncor and Syncrude

Canada, Ltd. both began with the first approach, with Suncor converting to large-scale truck and shovel technology in 1993. Underground mining options have also been proposed, but have been largely rejected for the time being due to the risk of the formation collapsing on any operators or equipment. This option, however, should not be dismissed out of hand because a novel aspect or the developer's requirements (which eliminate the associated dangers) may make it acceptable.

After the oil sand is extracted, the bitumen must be recovered. The hot water process is used to accomplish this. To date, the hot water process is the only commercially successful method of recovering bitumen from mined oil sand in North America. Many process alternatives have been tested with varying degrees of success, and one of these alternatives may eventually replace the hot water process. The hot water process takes advantage of the linear and nonlinear variations in bitumen density and water density with temperature, respectively, so that bitumen, which is heavier than water at room temperature, becomes lighter than water at around 80°C (180°F). Surface-active materials in oil sand also play a role in the process.

The oil sands deposits in the United States and the rest of the planet have received far less attention than the deposits in Canada. Nonetheless, approaches to recovering bitumen from US oil sands have been developed. In the current situation, an effort has been made to develop a hot water process for the Utah sands. Because of the oil-wet Utah sands, as opposed to the water-wet Canadian sands, the process differs significantly from that used for the Canadian sands. This necessitates disengagement via hot water digestion in a high-shear force field under appropriate pulp density and alkalinity conditions. Aeration and froth flotation can also be used to recover the dispersed bitumen droplets.

The other above-ground method of separating bitumen from oil sands after mining involves direct heating of the oil sand without first separating the bitumen (Gishler, 1949). As a result, the bitumen is not recovered as such, but rather transformed into an upgraded overhead product. Although several methods have been proposed, the common thread is heating the oil sand to separate the bitumen as a volatile product. However, at this time, it must be recognised that the bitumen's volatility is extremely low, and what actually separates from the sand is a cracked product with the coke remaining on the sand. The coke formed as a result of the bitumen's thermal decomposition remains on the sand, which is then transferred to a vessel for coke removal by burning in air. The hot flue gases can be used to heat incoming oil sand or to fuel refineries.

A later proposal suggested that the Lurgi process could be used to convert bitumen (Rammler, 1970). A more modern method of cracking the bitumen constituents on the sand has also been developed (Taciuk, 1981). The processor is made up of a large, horizontal, rotating vessel divided into compartments. A preheating zone and a reaction zone are the two major compartments. Product yields and quality are said to be excellent (Figure 11.1).

Processes involve the reaction of heavy crude oils with an external source of hydrogen, resulting in an increase in the hydrogen-to-carbon ratio overall. All upgrading technologies can be classified as follows within these broad categories:

Carbon rejection: visbreaking, steam cracking, fluid catalytic cracking, and coking, for example. Carbon rejection processes are appealing methods of bitumen conversion because they allow for low operating pressure, despite a high operating temperature, and do not require expensive catalysts. Hydrogen addition processes include catalytic hydroconversion (hydrocracking), hydrovisbreaking, and donor solvent. Desulfurization to low-sulfur feedstocks for other processes or hydrocracking to kerosene and gas oil are offered by bitumen hydrotreating processes (with the associated process parameters

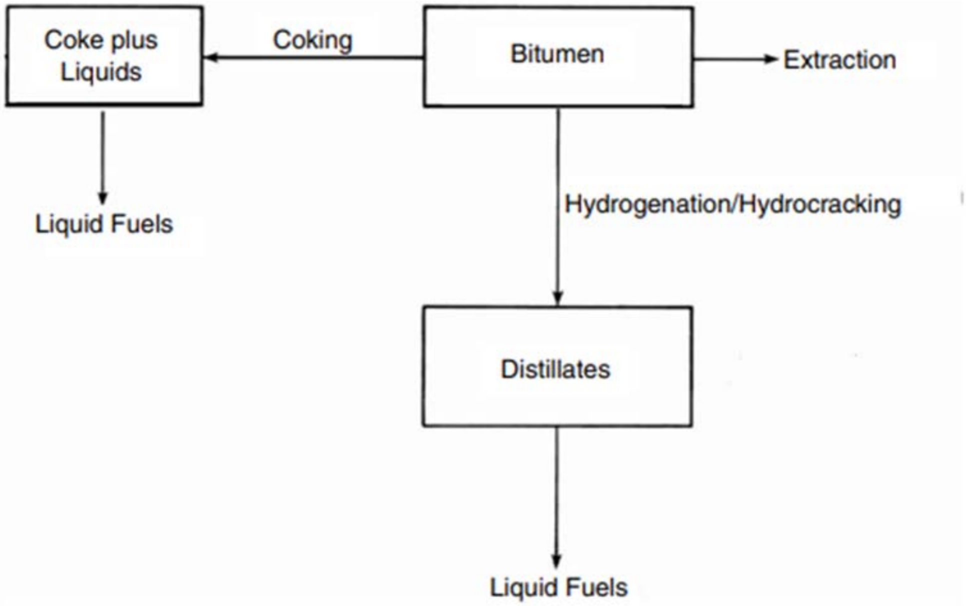

Figure 11.1 Represent the liquid fuels from oil bitumen.

Distillation and deasphalting are two separation processes. Solvent deasphalting removes sulphur and nitrogen compounds, as well as metallic constituents, from high-carbon asphalt and is better suited for use in conjunction with other processes. Currently, the overall upgrading process for bitumen to liquid fuels is completed in two steps. The primary upgrading or primary conversion process improves the hydrogen-to-carbon ratio by either carbon removal or hydrogen addition, cracking bitumen to produce distillable products that can be processed downstream to liquid fuels more easily. The secondary upgrading process involves hydrogenation of the domestic production and is used to remove sulphur and nitrogen from the primary products.

The upgraded or synthetic crude are then refined into a wide range of liquid fuels, including gasoline, diesel fuel, and jet fuel. Bitumen is deficient in hydrogen and must be upgraded through carbon removal (coking) or hydrogen addition (hydrocracking). Bitumen conversion can be accomplished in two ways: (1) by direct heating of mined oil sand and (2) by thermal decomposition of separated bitumen. The latter is the commercial method, but the former is worth mentioning because the possibility of commercialization remains.

Although the improvements in properties may not appear to be dramatic, they usually result in significant benefits for refinery operators. Any incremental increase in the units of hydrogen-to-carbon ratio can save significant amounts of expensive hydrogen during the upgrading process. The same principles apply when reducing the nitrogen, sulphur, and oxygen contents. This latter occurrence improves catalyst life and activity while also lowering metal content. In short, while in situ recovery processes are less efficient in terms of bitumen recovery compared to mining operations, they may have the additional benefit of leaving some of the more noxious constituents (from the processing objective) in the ground. The low proportion of volatile constituents (those boiling below 200°C [392°F]) in bitumen precludes distillation, and it is acknowledged that refining by thermal means is required to produce liquid fuel streams. A variety of factors have influenced the development of facilities that can convert bitumen into synthetic crude oil.

Visbreaking has been considered as one of the primary upgrading processes. A visbreaking product, on the other hand, is still high in sulphur and nitrogen, with some degree of unsaturation. This latter property promotes gum formation, which increases the risk of pipeline fouling and other disposal issues in storage facilities and fuel oil burners. A high sulphur content in finished products is unacceptably harmful to the environment. Furthermore, high nitrogen levels cause issues in downstream processes, such as catalytic cracking, where nitrogen levels in excess of 3000 parts per million cause rapid catalyst deactivation; metals (nickel and vanadium) cause similar issues.

Higher-boiling constituents (those boiling between 200 and 400°C [390 and 750°F]) can be isolated by distillation, but more than 40% of oil sand bitumen boils above 540°C (1000°F). Despite this, the low proportion of volatile constituents (those boiling below 200°C). Distillation to an appropriate cut point could yield a product of acceptable quality, but the majority of the bitumen would be left behind to be refined by whatever means were necessary, keeping in mind the need to balance fuel requirements and coke production. As a result, any bitumen-upgrading programme must convert the nonvolatile residue to a lower-boiling, low-viscosity, low-molecular-weight product with a high hydrogen-to-carbon ratio.

Coking Processes

Coking processes are the primary upgrading processes used to convert bitumen to distillable products. Coking was the process of choice for bitumen conversion in the early stages of oil sand development, and bitumen is currently converted commercially by delayed coking (Suncor) and fluid coking (Syncrude). The charge is converted to distillate oils, coke, and light gases in each case. Plant fuel can be made from the coke fraction and product gases. The coker distillate is a partially upgraded material that can be used to feed hydrodesulfurization to produce low-sulfur synthetic crude oil. Delayed coking is a semibatch process in which feed bitumen is heated before being fed into coking drums with enough residence time for cracking reactions to occur. The Suncor plant (in operation since 1967) employs a delayed coking technique followed by distillate hydrotreating to produce synthetic crude oil with properties that differ significantly from the original bitumen but are similar to those of conventional petroleum. At the time of planning (from 1960 to 1964), the choice of delayed coking over less severe thermal processes such as visbreaking was based on the high yields of residuum produced in these alternate processes. The coke yields from the residuum would have exceeded the plant fuel requirements, especially if the distillate had to be shipped elsewhere for hydrogen treatment, as well as a better product distribution and properties. Alternative disposal routes for excess coke would be required (at Suncor, bitumen conversion to liquids is on the order of 75% by volume, with fluid coking yielding a generally higher yield of liquids than delayed coking). The rest is made up of coke (about 15% by weight) and gases.

Fluid coking is a continuous process that involves two vessels filled with fluid coke. It produces more overhead products than delayed coking. Feed oil flows into the reactor vessel, where it cracks and forms coke, which is then burned in the burner. The coke circulation required for heat balance is provided by fluid transfer lines between these vessels. The amount of coke burned is just enough to cover heat losses and provide heat for the cracking reactions. Whole bitumen (or topped bitumen) is preheated and sprayed into the reactor, where it is thermally cracked in the fluidized coke bed at temperatures ranging from 510 to 540°C (950 to 1000°F) to produce light oil. Products and Coca-Cola. The coke is deposited on the fluidized coke particles, while the light products are carried overhead to a scrubbing section, where any high-boiling products are condensed and reassembled with the reactor fresh feed. The uncondensed scrubber overhead flows into a fractionator, which extracts liquid products with suitable boiling ranges for downstream hydrotreating. Cracked reactor gases, which contain butanes and lower-molecular-weight hydrocarbon gases, are carried overhead to a gas recovery section. The propane material eventually flows to the refinery gas system, where the condensed butane and butenes can be combined only with synthetic crude (subject to vapour pressure limitations). The heat required to vaporise the feed and provide reaction heat is supplied by hot coke circulated back to the reactor from the coke heater. Excess coke formed from fresh feed and deposited on hot circulating coke in the fluidized reactor bed is withdrawn from the reactor bottom (after steam stripping). As with direct coker distillates, sulphur is distributed throughout the boiling range of the delayed coker distillate. Nitrogen is more concentrated in the higher-boiling fractions, but it is present in the majority of the distillate fractions as well. Raw coker naphtha contains a high concentration of olefins and diolefins, which must be saturated via downstream hydrotreating. The gas oil contains a high aromatic content, which is typical of coker gas oils.

Product Upgrading

After that, the primary liquid product is hydrotreated (secondary conversion or refining) to remove sulphur and nitrogen (as hydrogen sulphide and ammonia, respectively) and hydrogenate the unsaturated sites exposed by the conversion process. Light distillates and medium-to-heavy fractions may require separate hydrotreaters; for example, heavier fractions require higher hydrogen partial pressures and operating temperatures to achieve the desired degree of sulphur and nitrogen removal. To achieve the required product quality and process efficiency, commercial applications have relied on the separate treatment of two or three distillate fractions at the appropriate severity.

Hydrotreating is typically done in down-flow reactors with a fixed bed of cobalt molybdate catalysts. The produced hydrogen sulphide and ammonia are removed from the reactor effluents. Any light ends are routed to the fuel gas system, where the liquid byproducts are recombined to create synthetic crude oil. The liquid products are finished and stabilised (hydrodesulfurization and saturation) by hydrotreating the liquid streams as two or three separate streams. This is required due to the differences in the conditions and catalysts required for treating a naphtha fraction versus the conditions required for treating gas oil. It is more efficient to separate the liquid product streams and then blend the finished liquids to produce synthetic crude oil. Suncor coker distillate is treated as three separate fractions to take advantage of optimal operating conditions for various distillate fractions: naphtha, kerosene, and gas oil.

Syncrude's operation separates bitumen products into two distinct fractions: naphtha and mixed gas oils. Each plant combines hydrotreated fractions to produce synthetic crude oil, which is then piped to a refinery. The upgraded or synthetic oil production has properties that differ significantly from the original feedstock and are more similar to those of a conventional high-API gravity crude oil. Several other processes for bitumen upgrading have received some attention. Partially upgrading (a type of thermal deasphalting), flexicoking, the Eureka process, and various hydrocracking processes are among them.

Gishler tested direct coking of tar sand using a fluid bed technique. In this process, tar sand is fed into a coker or still, where it is heated to approximately 480°C (895°F) by contact with a fluid bed of clean sand from which the coke has been burned away. The bitumen's volatile components are distilled. Thermal cracking of residual portions results in the deposition of a layer of coke around each sand grain. Coked solids are withdrawn through a standpipe, fluidized with air, and transferred to a burner or regenerator (operating at 800°C, 1470°F), where the majority of the coke is burned off the sand grains. A standpipe is used to extract the clean, hot sand. A portion (20 to 40%) is rejected, and the remainder is recirculated to the coker to heat the coking reaction. The byproducts exit the coker as vapour, which condenses in a receiver. The receiver's reaction off-gases are recirculated to help fluidize the clean, hot sand that is returned to the coker.

An early process used a coker to convert bitumen and a burner to remove carbon from the sand. A later proposal suggested that the Lurgi process could be used to convert bitumen. Another method for cracking the bitumen constituents on the sand has also been developed. The processor is made up of a large, horizontal, rotating vessel divided into compartments. A preheating zone and a reaction zone are the two major compartments. The partial coking or thermal deasphalting process improves bitumen only slightly. The hot water process froth is distilled at atmospheric pressure in partial coking, and minerals and water are removed. The result is a dehydrated mineral-free bitumen product containing the majority of the asphaltenes and coke precursors. The process was carried out in batch equipment in laboratory tests ranging from 30 minutes to 4 hours. When the liquid temperature exceeds 340°C (645°F), thermal cracking begins. The distillation is continued to temperatures ranging from 370 to 450°C (700 to 840°F). The coke production rate is approximately 1% by weight of feed per hour with slow heating (10°C [50°F] temperature rise per hour). As coke forms around the entrained mineral particles, 1 to 4% by weight coke is recovered as distillate, and up to 50% by volume of the feed is recovered as distillate. Following this treatment, the residue can be filtered to produce an essentially ash-free product suitable for applications such as metallurgical coke or the production of bituminous paints, which would have been ineligible due to the original mineral content.

A gasifier vessel is added to the system during flexicoking to gasify excess coke with a gas-air mixture into a low-heating-value gas that can be desulfurized and used as a plant fuel. The Eureka process is a delayed coking variant that employs steam stripping to increase yield and produce heavy pitch rather than coke by-product. Another option is to use steam as an agent to reduce coke formation. Thermal cracking of Athabasca bitumen at various reaction conditions with and without the presence of steam, for example, revealed that the presence of steam reduced coke yield, reduced sulphur removal, and reduced the H/C ratio of the liquid products. Hydrocracking has also been proposed as a method of bitumen upgrading, i.e., the conversion of asphaltene to liquid fuels (Solari, 2000). Direct hydrogenation or hydrocracking of bitumen produces significantly more liquid than coking, and significant amounts of sulphur and nitrogen are removed. However, large amounts of external fuel or hydrogen plant feedstock are currently required. Most hydrocracking processes begin with an up - flow reactor system that cracks or converts the 524°C (975°F) material.

To meet the challenge of these heavy feedstocks, the future of bitumen upgrading lies in the development of new processes and the evolution of refinery operations. Indeed, upgrading heavy oil and bitumen, particularly residua, is a critical step for refineries. Indeed, the petroleum industry is concerned about the increasing supply of heavy crude oil. Significant investments in refining conversion processes will be required to profitably utilise these heavy crude oils in order to meet the changing pattern of product demand. The most efficient and cost-effective solution to this problem will be determined by individual country and company circumstances. The most promising technologies, however, will almost certainly involve the conversion of vacuum bottom residual oils, asphalt from deasphalting processes, and superheavy crude oils into useful low-boiling and middle-distillate products.

New bitumen conversion processes will most likely replace the current visbreaking (or hydrovisbreaking) and coking methodologies, with some degree of hydrocracking as a primary conversion step. In many refineries, other processes may replace or supplement the deasphalting processes. The upgrading of bitumen from oil sand deposits in Canada is an exception that may become the rule. Without prior distillation or topping, the bitumen is subjected to either delayed coking (Suncor) or fluid coking (Syncrude) as the primary upgrading step. The product streams are hydrotreated and combined after primary upgrading to form synthetic crude oil, which is shipped to a conventional refinery for further processing. Other heavy oils and bitumen could theoretically be upgraded in the same way and, depending on the upgrading facility, upgraded further for sale.

The processing limitations of heavy oil and bitumen are largely determined by the amount of higher-molecular-weight constituents (i.e., asphaltene constituents) that contain the majority of the heteroatom core supporters. These constituents are responsible for high thermal and catalytic coke yields. Asphaltenes are associated with the majority of the metal constituents in crude oils. Some of these metals can combine to form organometallic complexes. The remaining elements are found in organic or inorganic salts that are soluble in water or crude oil. Attempts have been made in recent years to isolate and study the vanadium present in petroleum porphyrins, primarily asphaltene fractions.

Complex molecules (such as those found in the original asphaltene fraction) or those formed during the process are not sufficiently mobile (or are too strongly adsorbed by the catalyst) to be saturated by hydrogenation when catalytic processes are used. The government of Alberta, Canada, has announced a standard royalty formula for the oil sand industry, having embraced the principles and, to a large extent, put into practise, the fiscal recommendations of the National Task Force on Oil Sands Strategies. The Canadian government intends to broaden mining taxation to include in-situ operations. More than $3.4 billion ($3.4 109) in new projects and expansions have been waiting for fiscal terms to be resolved in order for the industry to move forward with a number of projects in the early stages of development. Such a move is expected to encourage further advancement of Canada's oil sands resources.

Shell has built an upgrader near Fort Saskatchewan, Alberta, in another step towards the future. The upgrader processes bitumen using hydrogenation technology to produce a wide range of premium-quality low-sulfur liquid fuels.

Pipelines transport diluted bitumen to the upgrader. There have been numerous forecasts of global production and demand for conventional crude over various time periods. Even after accounting for the impact of the conservation ethic, the development of renewable resources, and the possibility of slower economic growth, nonconventional sources of liquid fuels may be required to compensate for future anticipated shortfalls in conventional supplies.

This is especially true in North America, where there are even more compelling reasons to develop viable alternative fossil fuel technologies. These reasons include, of course, supply security and the urgent need to reduce the impact of energy costs on the balance of payments. There has been hope that developing technology in North America will eventually succeed in applying new areas of nuclear and solar energy to the population's energy demands. However, the optimism of the 1970s has been replaced by the reality of the 1980s, and it is now clear that these energy sources will not be the solution to energy shortages for the rest of the century. More liquid fuels from fossil fuel sources will almost certainly be required to meet energy demands.

In the United States, the economics of oil sands are still largely speculative. Estimates for current and posited Canadian operations are, in some ways, inapplicable to operations in the United States because different production techniques may be required. There is no doubt that extracting energy from oil sands is a difficult and costly process. With conventional production, the search is a gamble, and the costs can be high with no guarantee of a commercial find. The bitumen is known to be present in oil sand deposits, but extracting it has been difficult, necessitating a large investment in untested technology. There is no real market for the bitumen extracted from the oil sand, and the oil sand itself is too bulky to ship elsewhere with any hope of a profit. As a result, the extraction and upgrading plants must be built in close proximity to the mining operation.

To develop the current concept of hydrocarbons from oil sands, three operations must be combined, each of which adds significantly to the cost of the product. The government of Alberta, Canada, has announced a standard royalty formula for the oil sand industry, having embraced the principles and, to a large extent, put into practise, the fiscal recommendations of the National Task Force on Oil Sands Strategies. The Canadian government intends to broaden mining taxation to include in-situ operations. More than \$3.4 billion (\$3.4 109) in new projects and expansions have been waiting for fiscal terms to be resolved in order for the industry to move forward with a number of projects in the early stages of development. Such a move is expected to encourage further development of Canada's oil sands resources. Shell has built an upgrader near Fort Saskatchewan, Alberta, in another step towards the future. The upgrader processes bitumen using hydrogenation technology to produce a wide range of premium-quality low-sulfur liquid fuels. Pipelines transport diluted bitumen to the upgrader.

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To develop the current concept of liquid fuels from oil sands, three operations must be combined, each of which adds significantly to the cost of the venture: (1) a mining operation capable of handling 2 million tonnes or more of oil sand per day, (2) an extraction process to separate the bitumen from the sand, and (3) an extraction process to separate the bitumen from the sand. Suncor (previously Great Canadian Oil Sands Ltd.) was the first of the Potential oil sands developers brought with them a number of drawbacks. The technical issues were complex and numerous, resulting in Suncor (on stream: 1967) accruing a $67 million deficit by the end of 1976, despite reporting a $12 million profit for that year. Suncor has reported consistent profits since then, and has even recognised the opportunity to expand operations to 60,000 barrels per day of synthetic crude oil. However, in retrospect, such a situation appears to have some distinct advantages. Suncor's early entry into oil sand processing resulted in a low capital cost per daily barrel for a nonconventional synthetic crude oil operation. Total capital costs were around $300 million, which equates to about $6000 per daily barrel at a production rate of 50,000 bbl/d.

It is worth noting here that a conventional refinery (150 to 300 103 bbl/d) could have cost $100 to $400 million at the time, with an energy balance (i.e., energy output/energy input) in excess of 90%. An oil sand refinery of the Suncor-Syncrude type could have an energy balance of 70 to 75%. The capital costs for the second oil sand processing plant, built by Syncrude Canada Ltd., were significantly higher. In fact, it was the rapidly rising capital costs that nearly brought the Syncrude project to a halt. Capital requirements, which were initially estimated to be less than $1 billion (i.e., $1 109), began to skyrocket in early 1975. The cost was higher than one of the four partners was willing to pay, so the number of participants was reduced to three. Because the company leaving held one of the largest stakes, the loss was felt acutely, and the project was temporarily jeopardised. It was eventually saved thanks to the participation of the Canadian government as well as the governments of Ontario and Alberta. The Canadian government invested 15% of the project's total cost, with Alberta investing 10% and Ontario investing 5%. The remaining funds were held by three of the original participants: Imperial Oil Ltd., Gulf Oil Canada Ltd., and Canada-Cities Service Ltd. Following that initial setback, progress was rapid, and the project (located a few miles north of the Suncor plant) was completed (onstream: 1978). The latest cost estimate for the plant is in the $2.5 billion range. The capital cost per daily barrel exceeds $20,000 at a design level of 120,000-130,000 bbl/days.

The investment for both the Suncor and Syncrude plants is divided into four categories: (1) mining (28 to 34%), (2) bitumen recovery (approximately 12%), (3) bitumen upgrading (28 to 30%), and (4) offsites, including the power plant (16 to 24%).] Obviously, there are numerous factors to consider when developing oil sand resources for the production of liquid fuels. It is more important to recognise that what is important in the development of one resource may be less important in the development of another. Recognizing this aspect of oil sand development is a significant benefit that will aid in the production of liquid fuels in a cost-effective and efficient manner.

CHAPTER 12

BASICS OF SHALE OIL

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Since the 1970s oil embargo, there has been increased interest in retorting oil from oil shale to produce a competitively priced synfuel. Commercial interest, which was once very high in the 1970s and 1980s, significantly declined in the 1990s as a result of the stable and low oil price. However, interest in oil shale as a clean liquid fuel source is resurrecting in the twenty-first century, owing primarily to skyrocketing petroleum prices and a global oil shortage. However, it should be noted that oil shales have long been used as liquid - vapor fuels in certain areas, and research into them has a long history. Shale is a tough, dense rock that ranges in colour from light tan to black after being mixed with a variety of sediments over a long geological time period. Shales are commonly referred to as black shale or brown shale, depending on their colour. Oil shales are also known by various names in different parts of the world. The Ute Indians, for example, dubbed some outcroppings "the rock that burns" after observing them burst into flames when struck by lightning.

Oil shales are found all over the world, with known deposits on every continent. In this regard, oil shale differs significantly from petroleum, which is concentrated in certain parts of the world. displays some publicly available data on global oil shale reserves. The statistical values vary slightly depending on the data source and the year of reporting. Shales have previously been used as a source of liquid fuel in countries such as Scotland, Sweden, France, Namibia, Australia, the USSR, China, Brazil, and the United States.

However, the oil shale industry has seen several ups and downs due to political, socioeconomic, market, and environmental factors. It is thought (though evidence is lacking) that oil shales have been used directly as solid fuels in various regions, particularly in areas with rich shales readily available near the earth's surface. An oil shale deposit in Autun, France, for example, was commercially exploited as early as 1839. 62 Shale oil was promoted as a replacement for wood, on which America relied for energy as early as the 1850s. Prior to the discovery of crude oil in 1859, the oil shale industry in the United States was a significant part of the American economy. With the availability of vast supplies of inexpensive liquid fuel, i.e., petroleum, as Colonel Drake drilled his first oil well in Titusville, Pennsylvania, shale oil and its commercial production were gradually forgotten and virtually disappeared. Similarly, Scotland had a viable shale industry from 1850 to 1864, when it was forced to close due to the low price of imported crude oil. It's worth noting that British Crude oil (BP) was founded as a shale oil company. Similarly, in Russia, shale from Estonia used to supply fuel gas to Leningrad.

The Naval Petroleum and Oil Shale Reserves were established by executive order of the President of the United States in 1912. Since then, the US Department of Energy's Office of Fossil Energy has been in charge of overseeing the country's strategic interests in oil shale. The United States' interest in oil shale was revived briefly in the 1920s as domestic crude oil reserves declined.

However, subsequent discoveries of large amounts of oil deposits in Texas dashed the hopes of an emerging oil shale industry. Serious interest in oil shale commercialization and development resurfaced in the 1970s and 1980s, as the Arab oil embargo impacted global energy supply and, as a result, the global economy.

Unocal developed their Union B retort process in 1974, and in 1976 planned to build a commercial-scale plant at Parachute Creek when the investment was cost-effective. Exxon, Shell, Dow Chemical, Sohio, TOSCO ARCO, AMOCO, Paraho, and other companies began their own versions of oil shale development. Unocal began building their Long Ridge 50,000 bbl/d plant in 1981, based on their Union B retorting technology. In 1980 and 1981, AMOCO demonstrated in situ retorting of 1,900 and 24,400 bbl of shale oil, respectively. Exxon purchased ARCO's Colony interest in 1980 and began construction on Colony II in 1981, aiming for a production level of 47,000 bbl/d using the TOSCO II process. Exxon announced the cancellation of their Colony II project in 1982 due to low demand and high costs. Exxon Black Sunday was the name given to this occurrence. Shell, meanwhile, continued their in situ experiments at Red Pinnacle until 1983. To make matters worse, Congress terminated the Synthetic Liquid Fuels Program after 40 years of operation and a $8 billion investment. Paraho reorganised as New Paraho and began producing SOMAT asphalt. Occidental abandoned their C-b tract project in Rio Blanco County, Colorado, in 1991. Unocal operated their last large-scale experimental mining and retorting facility in the western United States from 1980 until 1991, when its Long Ridge (San Miguel County, Colorado) project was shut down.

Over the course of the project, Unocal produced 4.5 million barrels of shale oil from oil shale, averaging about 34 gal of shale oil per tonne of rock. There has been no oil shale production in the United States since Unocal's closure in 1992. In the 1980s and 1990s, the stable crude oil price was once again the primary reason for the decline in interest in oil shale. Shell maintained some efforts in oil shale, particularly in the area of this in situ heating technology at their Mahogany, Colorado property. In 1997, a notable experiment on in situ heating was carried out. Although oil shale activities in the United States have essentially ceased, significant efforts have continued in other countries such as Estonia, Australia, and Brazil.

There is a renewed interest in oil shale in the twenty-first century, as most developed regions of the world experienced unstable and high energy prices, including those for natural gas and petroleum products, at the start of the new century. Examples of energy-related crises include: (1) blackouts in California in 2001, (2) gasoline price increases in various regions of the United States in 2000 and 2001, (3) extremely high gasoline prices due to a lack of crude oil supply in 2004, (4) extremely high crude oil prices in 2005 and 2006, and (5) sharp increases in residential energy costs in 2000, 2001, 2005, and 2006. It remains to be seen, however, whether the desire for energy identity or independence will tip the scales back in favour of developing western U.S. oil shales.

Oil shale is currently commercially exploited in several countries, including Brazil, China, Estonia, and Australia. Brazil has a long history of oil shale development and exploitation dating back to the late 1800s. Shale oil was first produced in 1935 at a small plant in So Mateus do Sul, Paraná. Petrobras imitated a more serious development effort by developing the Petrosix process for oil shale retorting. The Semiworks retort was developed in 1972 and operated on a limited commercial scale until December 1991, when a larger Industrial Module Retort was put into service for commercial production. In 1999, Brazil's total annual shale oil production was 195,200 tonnes.

In China, total annual shale oil production in Fushun, Liaoning province, was 80,000 tonnes in 2001.

They employed 80 new retorts known as Fushun retorts. Fushun used to produce up to 780,000 tonnes of shale oil per year using the older retorts, and output peaked in 1959. China Power Investment Corp (CPIC), one of the country's major power producers, is also planning a major development effort in Jilin province. The estimated oil shale deposit in Jilin province is 17 billion tonnes, accounting for approximately 56% of total deposits in China. According to some, China has the world's fourth largest oil shale deposits, trailing only the United States, Brazil, and Russia.

Estonia has a long history of developing and commercialising oil shale. Its deposits are located in the west of the Baltic Oil Shale Basin and contain high-quality oil shale. Permanent oil shale mining began in 1918 and continues to this day. In 1980, Estonia's oil shale output peaked at 31.35 million tonnes. Output in 1999 was 10.7 million metric tonnes, with 1.3 million tonnes retorted to produce 151,000 tonnes of shale oil. The Energy Security Act, S.932, was enacted in the United States on June 30, 1980, during the Carter administration. This legislation was intended to help create 70,000 jobs per year in the design, construction, operation, and supply of resources for synfuel plants and biomass fuel production. The Synthetic Fuels Corporation was established by the act.

President Reagan's new policies, combined with relatively stable oil prices, made the synfuel industry less appealing to the general public. Production and development of synfuels became less strategic under President Bush's administration, in favour of clean coal technology (CCT) and acid rain control.

When energy prices were very stable and low during the Clinton administration, this de-emphasizing trend intensified in favour of national budget deficit reduction, which received public support and was based on projected long-term stability in energy supply and cost. Environmental protection has received widespread political and public support. Because of record-high energy prices and frequent shortages in the twenty-first century, President Bush has revived interest in energy self-sufficiency and commercial oil field development, but at the expense of some potential environmental disturbances. The US Department of Energy's Office of Naval Petroleum and Oil Shale Reserves initiated a study on the significance of America's oil shale resources in 2004. The United States also launched a new oil shale programme in 2006 with the Oil Shale Development Act of 2005, which established a leasing programme. Similarly, global interest in alternative energy has increased.

By the late 1920s, oil and gas, or fluids derived from fossil fuels, accounted for one-third of total energy consumption in the United States. By the mid-1940s, oil and gas were providing half of the United States' energy needs. They currently meet three-quarters of the United States' energy needs. The high demand for oil and gas is expected to last for some time, despite the fact that bioenergy and hydrogen fuels are rapidly gaining popularity and are widely regarded as the primary energy sources of the future.

As a result, with no new major petroleum deposits in sight, modern society's unprecedented appetite for fluid-type energy sources will necessitate supplementing domestic energy supplies with synfuels such as those derived from oil shale or coal, as well as alternative fuel sources such as biomass, crops (e.g., soy and corn), and recycled materials. Hydrogen and ethanol will undoubtedly play critical roles in the future energy market as new gaseous and liquid fuels.

Constraints In Commercial Production Of Shale Oil

Various constraints that represent potential deterrent factors can be encountered during commercialization of shale oils. These constraints are caused by a variety of factors, including technological, economic (or financial), institutional, environmental, socioeconomical, political, and water availability. Given the state of knowledge and the regulatory regime of the early 1980s, the Office of Technology Assessment (OTA) analysed the requirements for achieving each of the production goals by 1990. OTA identified the factors that could impede goal attainment. Their original target year of 1990 has been used without modification in this table. Given that no serious commercialization activity occurred in the 1990s for a variety of reasons, readers should use their own discretion in interpreting the provided information.

The constraints classified as "moderate" will impede but not necessarily prevent development; those classified as "critical" may become more serious barriers; and when it was ambiguous whether or not certain factors would impede development, they were classified as "possible" constraints. Despite the fact that the information in this table is now outdated, it is still relatively accurate and applicable to the current situation, given the relative inactivity in this field during the last decade of the twentieth century. Because of the high and fluctuating prices of energy, particularly liquid fuels, in the twenty-first century, there is renewed interest in our commercial viability of oil shale processes around the world.

Economic And Financial Constraints

Even though constructing a large-capacity oil shale plant is expensive, the product oil must be competitive in the current and destiny energy price structures. For the past four decades, global petroleum prices have fluctuated, and crude oil prices have risen sharply in the early twenty-first century. However, future pricing strategies of trying to compete fuels may have an impact on the industry's long-term profitability. This worry raises the risk level of the oil shale industry. Given the global energy market's scarcity of clean solvent fuel sources and the general trend of rising prices, the marketability of oil shale is improving, with promising future prospects. This could be especially true in countries with insufficient petroleum production but vast deposits of oil shale. There are three possibilities in this regard:

First, government involvement can improve the economic scenario by providing incentives and credits in various forms and tying the industry to the economic development of a region; second, specialisation of products and diversification of by-products can contribute to industry profitability; and third, securing captive use of shale oil in strategically developed energy-intensive industries can also contribute to industry profitability.

Despite the difficulty of estimating a generalised cost breakdown of shale oil production, a typical cost allocation for an oil shale project can be estimated. The table shows that mining costs account for a significant portion of total operating costs. The cost of obtaining shale oil crude, which includes mining and retorting, accounts for roughly 70% of the total operating cost. Most oil shale processes have energy efficiencies ranging from 58 to %, which can be improved further by using efficient motors, implementing creative energy integration schemes, and utilising waste energy.

efficiencies of various synfuel processes. It should be noted that efficiencies are extremely difficult to compare on a fair basis because efficiencies reported for the same process can vary greatly depending on who reports it, how it is measured, on what basis it is calculated, and so on.

Improving energy efficiency without increasing capital and operational costs is thus a critical task that the process development team must undertake.

Environmental And Ecological Constraints

The oil shale deposits found in the Green River Formation in Colorado, Wyoming, and Utah are the largest and most studied in the United States. The oil in these deposits is estimated to be 800 billion barrels of recoverable shale oil. This region has long been the most appealing to oil shale industries due to its vast resources and high oil content of shales. The technology used in the extraction and utilization of oil shale, on the other hand, has raised environmental and ecological concerns. The Appalachian and Rocky Mountains are dotted with Devonian-Mississippian eastern black shale deposits. Despite the fact that these oil shales are a significant source of fossil fuel, they are generally lower in grade (oil content for every unit mass of shale rock) than Green River Formation oil shales.

Physical And Transport Properties Of Oil Shale

Fischer Assay

The term Fischer assay of oil shale refers to the nominal amount of condensable oil that can be extracted from oil shale. The Fischer assay is a simple and representative quantity that can be easily obtained for all types of oil shale by following a standardised retorting procedure in a nitrogen atmosphere. The actual oil content in oil shale exceeds the Fischer assay, both theoretically and nominally. Oil yield from oil shale often outstrips the Fischer assay value by up to 50%, depending on the treatment processes and the type of oil shale. Retorting in a hydrogen-rich environment, retorting in a CO_2 sweep gas environment, supercritical fluid extraction of oil shale, and other such extraction processes are examples.

The oil shale Fischer assay procedure is adapted from a low-temperature carbonization of coal Fischer assay procedure. The Fischer assay procedure is described briefly below: Take a 100 g crushed sample of oil shale and subject it to a preprogrammed heating schedule (such as linear ramping) in an inert (such as nitrogen) environment. The oil shale is heated very linearly from 298 to 773 K over a 50-minute period while being expunged with nitrogen. The rate of linear heating is 9.5°C/min. Following the heat-up period, the sample is held at 773 K for an additional 20 to 40 minutes, and the oil collected is measured, typically in a condenser tube. This recovered oil is then measured in litres per tonne (l/ton) or gallons per tonne (gal/ton).

This method cannot recover all of the organic matter that was originally contained in shale and leaves char associated with ash in the rock matrix, as well as largermolecular-weight hydrocarbons that block the pores. Nonetheless, the Fischer assay is a very reusable solutions of recoverable organic hydrocarbon content that provides a common basis for comparison among different oil shales. If this value is greater than 100 l/ton, it is considered rich shale; less than 30 l/ton, it is considered lean shale.

Porosity

The porosity of porous materials can be defined in a variety of ways, depending on which pores are examined and how the void volumes are measured. They are as follows: interparticle porosity, intraparticle porosity, internal porosity, porosity by liquid penetration, saturable volume porosity, liquid absorption porosity, superficial porosity, total open porosity, bed porosity (sleeping void fraction), packing porosity, and so on.

Because the organic matter in the shale exists in solid form and is essentially insoluble, the porosity of the mineral matrix of oil shale cannot be determined using the methods used to determine the porosity of petroleum reservoir rocks.

Institute, Laramie, WY) discovered that inorganic particles have a micropore structure in the range of 2.36 to 2.66 vol%. Although the particles have a significant surface area, approximately 4.24 to 4.73 m2/g for shale assaying of 29 to 75 gal/ton, it appears to be limited primarily to the outer surface rather than the pore structure. the measured porosities of raw oil shales. Except for the two low-yielding oil shales, naturally occurring porosities in raw oil shales are almost non-existent and do not allow access to gases. Porosity may exist in the oil shale formation to some extent where fractures, faults, or other structural defects happened. It is also believed that a large portion of the pores are either blind or extremely difficult to access. Crackling and fractures, as well as other structural flaws, frequently create new pores and break up some of the blind pores. It should be noted that even at high pressures, closed or blind pores are normally inaccessible by mercury porosimetry. The instrument based on pressurised mercury penetration through pores is no longer used due to the severity of mercury poisoning.

Permeability

Permeability is the ability of a rock to transmit fluids, and it is typically measured in darcies or millidarcies. Permeability is a proportionality constant in Darcy's law, which relates fluid flow rate and viscosity to a static pressure applied to porous media. Darcy's law is a phenomologically derived foundational equation based on momentum conservation that describes fluid flow through a porous medium. The instantaneous discharge rate (local volumetric flow rate) through a porous medium is related to the local hydraulic gradient (change in hydraulic head over a distance, i.e., h/L, dh/dL, or h) and the hydraulic conductivity (k) at that point by a simple relationship.

$$Q = -kA\frac{h_a - h_b}{L}$$

where k′ denotes the intrinsic permeability with the dimension [length2]. Whereas [g/] describes the penetrating fluid properties, intrinsic permeability (k′) summarises the porous medium properties. The darcy (D), or more commonly the milli darcy or mD (1 darcy 10-12 m2), is the standard unit for permeability.

1 D is precisely equivalent to 0.986923 m2 when converted to SI units. The discussion presented here is simplified, focusing on unidirectional homogeneous fluid permeation without explicitly including any external force terms. However, it may still be obvious that permeability should indeed be expressed in a multidirectional manner; in other words, as a permeability tensor. Darcy's law is extensively discussed in most textbooks on transport phenomena, fluid mechanics, and hydraulogy. Because the pores are filled with a nondisplaceable organic material, the permeability of raw oil shale is essentially zero. Tisot demonstrated that at a pressure differential across the cores of 3 atm of helium for l min, gas permeability, either perpendicular or parallel to the bedding plane, was not detected in most oil shale samples. Oil shale, in general, is a highly impervious system. As a result, one of the most difficult aspects of any in situ retorting project is achieving a

suitable degree of permeability in the formation. As a result, an effective rubblization technique is critical to the success of an in situ pyrolysis project.

The relationship between porosity or permeability and temperature and organic content is of practical interest. When heated to 510°C, there is a noticeable increase in oil shale porosity. These porosities, which ranged from 3 to 6 1 vol%4 of the initial bulk oil shale volume, essentially represented the volumes occupied by organic matter prior to the extraction. where k′ is the intrinsic permeability with the dimension [length2]. Whereas [g/] describes the penetrating fluid properties, intrinsic permeability (k′) summarises the properties of the porous medium. The darcy (D) or, more commonly, the milli darcy (mD) (1 darcy 10-12 m2) is the standard unit for permeability.

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Electric Resistivity

In DC electric fields, measurements on various types of oil shales revealed an exponential decrease in resistivity values as both a function of temperature. The pattern is typical of ionic solids, which conduct current via a thermally activated transport mechanism. The presence of various nutrients in the oil shale rock matrix makes identifying the material's current-carrying ions difficult. The close correspondence of activation energies at high temperatures (>380°C) with those typically observed for carbonate minerals, on the other hand, appears to indicate that carbonate ions could be a major current-carrying species.

Estimates based on such data, however, are at best speculative and should be used with caution. The chemical change in oil shale material caused by heating could also have an effect on its conduction property. Thus, changes in the resistivity of Russian shales (from 1010 -cm at room temperature to 10 -cm at 900°C) were attributed to the thermal decay of oil shale kerogen. The frequency-dependent behaviour of electric resistivity as a function of reciprocal temperature (1/T) for a sample of raw Green River oil shale (117 l/ton Fischer assay). The resistivity curve minima are observed at temperatures ranging from 40 to 210°C, and they are caused by the gradual loss of free moisture and bonded water molecules to the clay particles in the shale matrix (Figure 12.1).

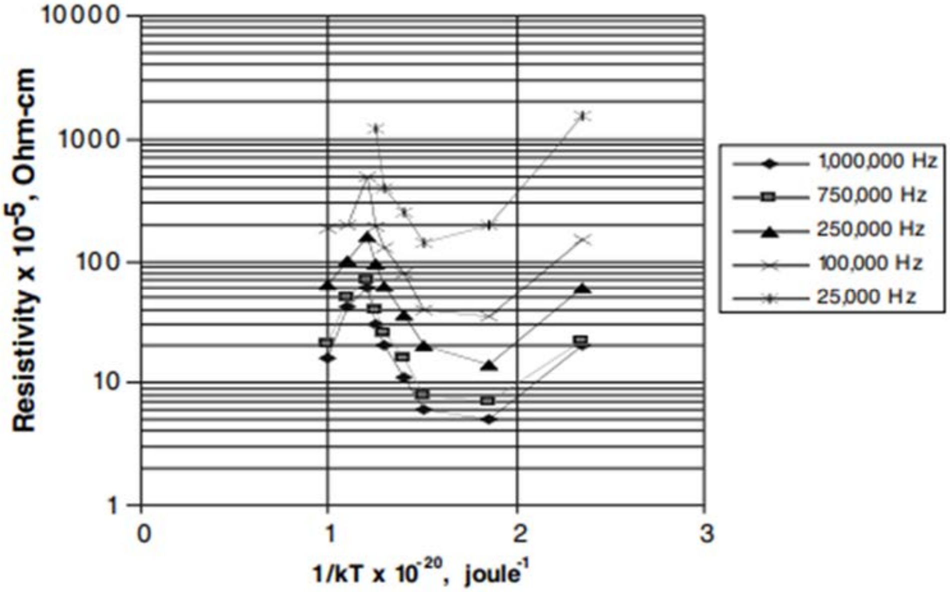

Figure 12.1 Represent the Frequency-dependent behavior of electrical resistivity as a function of reciprocal temperature.

For these reheating experiments, the strata were cooled to room temperature and then reheated to 500°C. As previously stated, the curves in exhibit the typical Arrhenius behaviour of ionic solids. There is no minimum or peak in the resistivity data, indicating that the results are due to thermally activated conduction.

Dielectric Constants

The dielectric constant (k) is a number that is a characteristic property that compares a material's ability to carry alternating current to vacuum's ability to carry alternating current. The capacitance created by the involvement of the material is thus directly related to its dielectric constant. Rajeshwar et al. provide a comprehensive review of the dielectric constant of oil shales. Oil shales' dielectric constant is also functionally dependent on temperature and frequency. According to Scott et al., abnormally high dielectric constants are observed for oil shales at low temperatures, and so these high values are attributed to electrode polarisation effects. 40 A more likely explanation is the presence of interfacial polarisation in these materials as a result of moisture and charge accumulation at the sedimentary varves in the shale.

Analytical Methods

precise analytical distillation may be required when characterising hydrocarbon mixtures for spec or other purposes. Actual distillation may necessitate between 25 and 100 plates. A reasonable-scale distillation is extremely expensive and time-consuming. Instead, a boiling point analysis can be obtained effectively using gas chromatography (GC) with a separating column at a constant temperature. However, this technique is limited to a relatively narrow boiling range because lighter components elute too quickly and tend to overlap, and heavy components emerge late and produce relatively wide bands or remain in the column. A newer technique for temperature programming the separating column allows for a broad-range, single-stage analysis.

The boiling range for varied peaks can be determined from elution times or temperatures of emergence by using a column packing that separates according to the boiling point and precise programming of the column temperature. The American Society for Testing and Materials has adopted a standard method for determining the boiling range of petroleum fractions using gas chromatography. The temperature must be programmed over a sufficient range to establish a retention time of at least l min for the IBP to dissolve the entire sample. A microsyringe is required for sample injection, and a flow controller is required to keep the carrier gas flow constant to l% across the entire operating temperature range. For a TCD, the carrier gas is either nitrous oxide or hydrogen, whereas a FID can use nitrogen, helium, or argon. The calibration mixture to be used is a mixture of hydrocarbons with known boiling points that cover the sample's boiling range. To obtain an accurate distribution of boiling range, at least one compound in the mixture must have a boiling point lower than the test sample's initial boiling point (IBP). The chromatographic data can be used to generate integral and differential plots. Most shale oils have density functions which are close to normal.

The pyrolysis reaction produces hydrocarbon vapour, which flows through a cyclone separator to remove entrained solids before entering a fractionation system similar to the primary fractionating column of a catalytic cracking unit. Heavy oil, distillate oils, naphtha, and light hydrocarbon gases are produced by oil vapour after this stage. The spent shale and ceramic balls are transferred from the retort to a cylindrical trammel screen. Spent shale flows into a surge hopper through screen openings. The ceramic balls pass through the screen and into a bucket elevator, where they are transported to the ball heater and reheated by direct contact with flue gas. After that, the ceramic balls are recycled back into the retort.

Spent shale is cooled in a rotating vessel containing tubes in which water is vaporised to produce high-pressure steam after it is discharged from the retort at 480°C. The shale is then pumped into another rotating vessel where it is cooled further by direct contact with water. The water flow is adjusted so that the vessel's spent shale contains 12% moisture by mass. Moisture is added to control dust emissions and make the spent shale compaction-ready before disposal. Oil shale is preheated by making direct contact between the crushed shale and the flue gas effluent from ball heater.

CHAPTER 13

THE UNION OIL RETORTING PROCESS

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The heat required for retorting in the Union Oil process is provided by the combustion of coke inside the retort. The shale is fed into the retort from the bottom and conveyed (pumped) upward by a specially designed rock pump. The product oil is recovered by syphoning it through the bottom of the retort. The method is quite unique and innovative, relying on well-designed rock pumps and a variety of designs for heating shales in the retort. According to Deering's process, coke-containing spent shale derived from a gas-heated reduction zone is passed countercurrently through a combustion-gasification zone to an upflowing mixture of steam and oxygen-containing gas to effect partial combustion of the coke on the spent shale, i.e., $C + 1\ 2\ O2 = CO$. The heat produced by combustion (exothermic heat) is used to support concurrent endothermic gasification reactions between steam and unburned coke, i.e., $C + H2O = CO + H2$.

The recycled water gas ($CO + H2O + H_2 + CO_2$) contains hydrogen and must pass through the combustion-gasification zone, where temperatures suitable for hydrogen combustion prevail. A significant part of the method is that, even with such passage, the overall yield of hydrogen is not significantly affected. This retort employs lump shales in the same size range as the Gas Combustion Retort. Another important aspect of the process is that no cooling water is required (Figure 13.1).

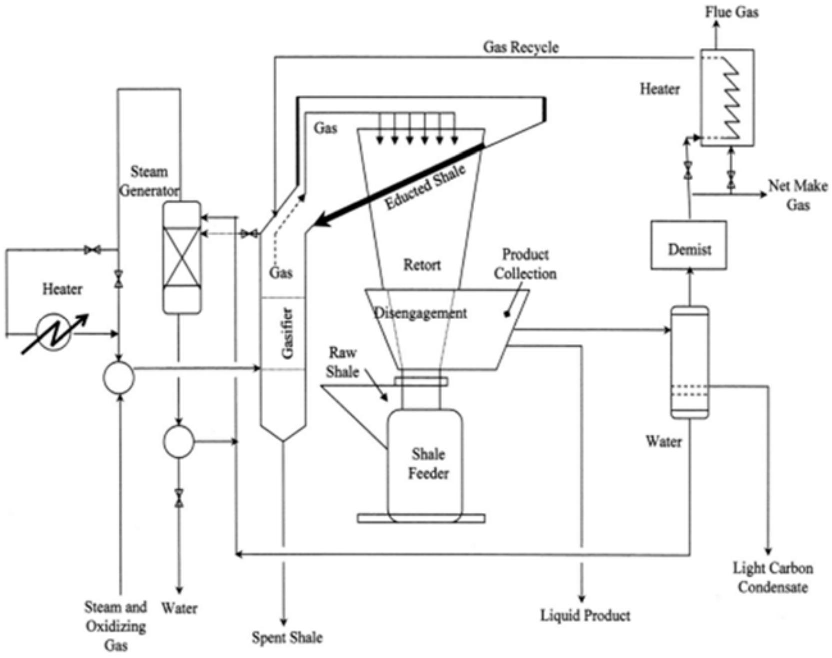

Figure 13.1 Represent the The Union Oil's retorting-gasification process.

The Lurgi-Ruhrgas Process

By bringing raw shale into contact with a hot fine-grained solid heat carrier, the Lurgi-Ruhrgas (LR) process distils hydrocarbons from oil shale. The spent shale is an ideal heat carrier for this process. Rich shales, on the other hand, typically deteriorate into a fine powder during process treatment and must be supplemented by more quality material like sand for use as heat carriers. In a mechanical mixer, such as a screw conveyer, the pulverised oil shale and heat carriers come into contact. The shale was first crushed to a maximum size of one fourth to one third of an inch in pilot plant tests, but larger commercial units may process particles as large as half an inch. A hot cyclone cleans the oil vapour and gaseous products of dust, and condensation separates the liquid oil.

The retorted shale from the mixer travels through a hopper to the bottom of a lift pipe with the cyclone dust. Preheated air created at the pipe's bottom transports the solids to the surge bin. The residual char in the shale is burned to heat the solids to around 550°C. In the event that residual char is insufficient for this process, fuel gas is also used. The hot solids separate from the combustion gases in the surge bin and return to the mixer, where they come into contact with fresh oil shale, completing the cycle. Kennedy and Krambeck introduced a new surge bin design as an improvement. Baffles in this improved surge bin allow for a more uniform flow of feed material through surge bin (Figure 13.2).

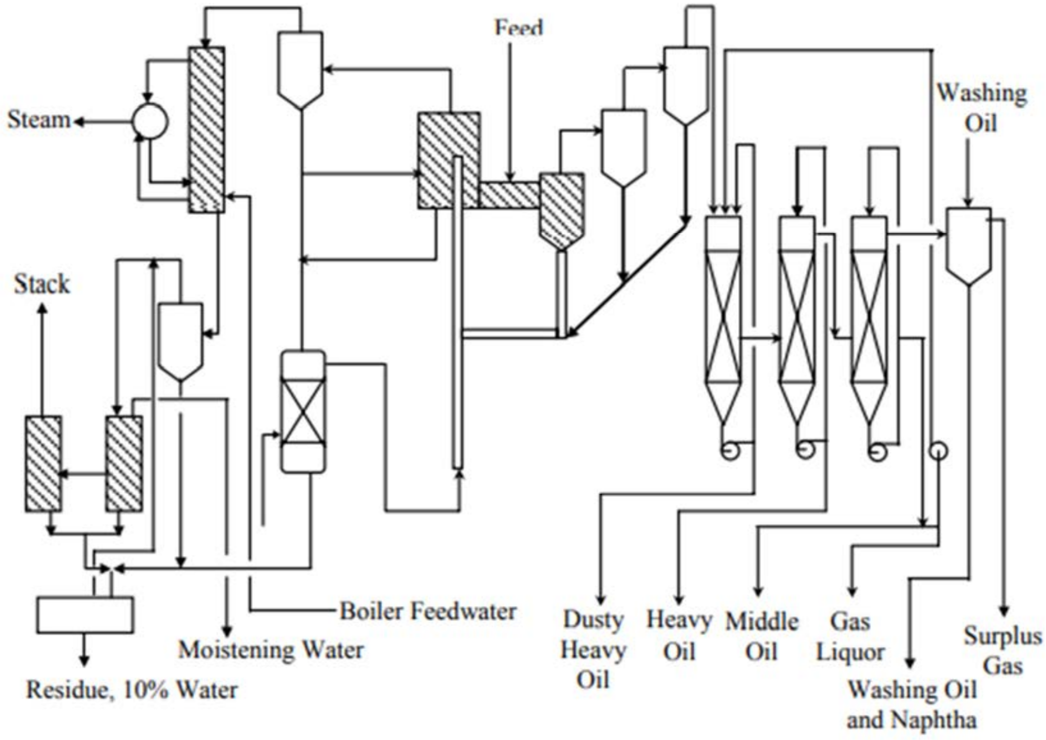

Figure 13.2 Represent the he Lurgi-Ruhrgas retort system.

Pilot plant tests have produced high yields, exceeding the Fischer assay value of the raw Colorado shale, at approximately 30 gal/ton of shale. As no combustion occurs in the mixer retort during this process, the product gas from the mixer has a relatively high calorific value (CV). The L-R process can operate with a wide range of particle sizes (very fine to medium) and, therefore, it can be modified for a variety of shale feedstocks. The process hardware is mechanically simple except for the mixer, which may be difficult to design because it must operate reliably in a harsh environment. However, the movement of dust through the system potentially causes two major problems of concern.

One is the accumulation of combustible dust in the transfer lines, increasing the likelihood of fires and plugging. The other is entrainment of dust in the oil produced. (Even though most of the dust is removed in the hot cyclone, some is inevitably carried over to the retort product.) When the crude oil from the process is fractionated, the dust concentrates in the heaviest fraction, requiring an additional processing step. This heavy fraction can be diluted and filtered or recycled to the mixer. The L-R process, originally developed in the 1950s for the low-temperature flash-carbonization of coal, was tested on European and Colorado oil shale in a 20 ton/d pilot plant at Herten, Germany.

Two 850 ton/d pilot plants for carbonizing brown coal were built in Yugoslavia in 19, and a large plant that uses the L-R process to produce olefins by cracking light oils was built in Japan. As an improvement over this process, time domain reflectometry (TDR) was evaluated and developed by Reeves and Elgezawi67 to monitor volumetric water content (θv) in oil shale solid waste retorted and combusted by the Lurgi-Ruhrgas process. A TDR probe was designed and tested that could be buried and compacted in waste embankments and provide in situ measurements for θv in the high-saline and high-alkaline conditions exhibited by the spent oil shale solid waste.

Superior's Multimineral Process

Superior Oil Co. invented the multimineral process. It produces minerals such as nahcolite (NaHCO3), alumina (Al2O3), and soda ash in addition to synthetic gas (syngas) and oil. s a schematic of Superior Oil's multimineral retort process The procedure is essentiall a four-step procedure for oil shale containing recoverable concentrations of oil, nahcolite, but instead dawsonite (a sodium-aluminum salt [Na3Al(CO3)3Al(OH)3]. Superior Oil had a pilot plant for this process in Cleveland, OH. Nahcolite is composed of discrete nodules that are brittler than shale. It is recovered through secondary crushing and screening, followed by photosorting, a specialised process that recovers nahcolite product with 80% purity. Shale is retorted using the McDowell-Wellman process after nahcolite is removed. Initially, the process was designed as a stirred-bed, low-Btu coal gasifier. The process's unique, continuously fed, circular-moving grate retort is a tried-and-true piece of equipment that provides accurate temperature control, separate process zones, and a water seal that eliminates environmental contamination.

Nahcolite has been tested as a dry scrubbing agent for sulfuric and nitrous oxide absorption. Dawsonite in shale is converted to alumina and soda ash in the retort. The alumina is recovered after the shale is leached with recycled liquor and makeup water from the saline subsurface aquifer. The liquid is seeded and the pH is lowered. This alumina can be extracted and recovered at a cost competitive with bauxite alumina. Evaporation recovers soda ash, which can be used in a variety of industrial applications such as neutralising agents. The spent shale is then leached and returned to the process. The byproducts produced by this process may make it more economically appealing (Figure 13.3).

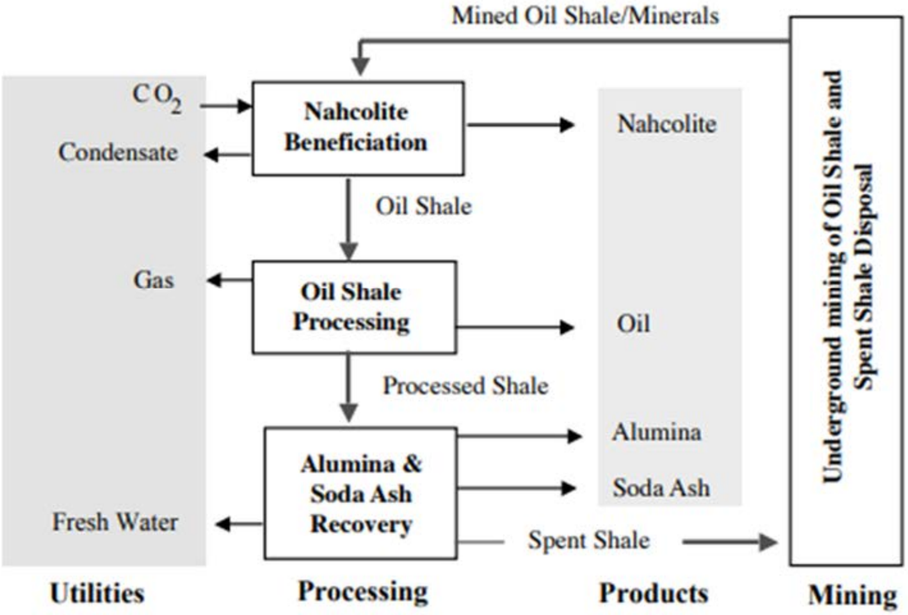

Figure 13.3 represent Superior oil's multimineral retort system.

The Paraho Gas Combustion Process

Paraho Development Corp. created the Paraho retort, a stationary, vertical, cylindrical, and refractory-lined mild steel kiln. A countercurrent flow of hot combustion gases brings raw shale to the retorting temperature at the top. Figure 1 depicts a schematic of the Paraho gas combustion retort system. Shale is fed into the retort from the top through a rotating "pantsleg" distributor. The rising hot gas stream degrades the kerogen into oil, gas, and residual char. The oil and gas are extracted, and the residual char burns in an air-gas mixture. Much of the sensible heat in the spent shale is recovered by injecting a portion of the gas-air mixture through the bottom of the kiln. The retort temperature is controlled by adjusting the gas-air mixture compositions in the preheat and combustion zones. 45 Shale oil vapours rise and pass through a moderately heated oil recovery unit. Shale oil and low-Btu gas are the end products. A typical crude shale oil analysis from this process. The produced shale oil can be enhanced to crude feedstock. The treated oil's heavy naphtha cut (88-178°C) has a higher octane rating and lower sulphur than a comparable Arab crude fraction. Because the diesel fraction (178-341°C) is identical to fractions from other sources, the heavy cut can be used as a feedstock for cracking units.

Fuel Flexibility

For equipment owners who choose to utilise CNG or LPG instead of gasoline, fuel flexibility is also an option. Both outcomes are possible with the installation of a separate fuel system and a fresh set of engine fuel injectors. Thus, owners of dual-fuel cars may drive on CNG and then switch to gasoline if there isn't a nearby CNG fuelling station when the gaseous fuel runs out. Alternative fuels may be used in non-road vehicles as well. It may be advantageous to use alternative fuels in ships, locomotives, agricultural machinery, mining equipment, and other types of vehicles. Internal combustion engines used in stationary vehicles may also run on alternative fuels. Industrial uses for stationary engines include producing electricity or extracting oil and gas. When power plant owners may choose between using conventional diesel, biodiesel, or natural gas in their facility, they can more easily achieve their operational and financial goals. For instance, reciprocating engine power generators may use natural gas to start their engines. The engines may be converted to biodiesel once they are operating, enabling net CO_2-free operation. Businesses that run fleets of cars must continuously choose between a number of goals, including lowering capital expenditures, operational expenses, fuel costs, and emissions, while also taking into account limitations on range and refilling. One or more of those goals may be advanced by switching to an alternate fuel.

Advantages of alternative fuels for the environment

A smart strategy to cut carbon emissions is to use alternative fuels. Carbon that was previously buried is released into the atmosphere when fossil fuels are burned. In contrast, the carbon that was removed from the atmosphere by the crops used to make biofuels is released. In light of this, biofuels are regarded as net-CO_2 free fuels. Similar to biofuels with negative carbon intensity, renewable natural gas fuel made from sewage gas or landfill gas might be considered.

Alternative fuels provide a range of possibilities for companies looking to lessen their carbon impact. Despite being fossil fuels, switching to CNG or LPG may significantly reduce CO_2 emissions. It may also be beneficial to use a gasoline with a higher ethanol or biodiesel component. Full conversions to biodiesel, hydrotreated vegetable oil (HVO), ethanol, renewable natural gas, even hydrogen, or an e-fuel may be an option for companies looking to cut their CO_2 emissions even further.

Internal combustion engines also release additional gases in their exhaust in addition to CO_2. The non-carbon emissions produced by the majority of corporations' fleets of vehicles should worry them. Alternative fuels that burn cleanly may be helpful here. Sometime investing in technology to reduce diesel exhaust pollutants is more cost-effective in the long term than, say, converting a diesel vehicle to operate on compressed natural gas. Non-carbon emissions can provide a unique set of issues in certain businesses. These issues might inspire revolutionary solutions built on an alternate fuel. For instance, a strong ventilation system is necessary to ensure a safe and breathing atmosphere in mines. This is no simple job with huge gear running beneath. That ventilation system's operation might be quite expensive and energy intensive. Numerous mining businesses have looked at hydrogen fueling possibilities as a result of these factors. Fueled by hydrogen, which produces zero pollutants, would need far less ventilation.

Advantages of alternative fuels economically

Although conventional fossil fuels like gasoline and diesel are often practical and economical, there are certain circumstances when alternative fuels are less expensive. When compared on a natural gas gallon equivalent basis, natural gas has consistently cost less than gasoline and diesel. By switching their fleets to operate on CNG, owners of garbage trucks, municipal buses, and other commercial vehicles have saved millions of dollars. Electricity and heat may be produced from biogas for the purpose of treating water.

Natural gas's cost is not only inexpensive, but it is also consistent throughout time. Prices for natural gas often don't fluctuate cyclically like those for fuels derived from petroleum, like gasoline. Owners of compressed natural gas cars benefit from reduced and more predictable running expenses as a consequence.

Upkeep and additional benefits of alternative fuels

There are several additional benefits of using alternative fuels. Here are some further advantages:

The following: Natural gas, propane, and hydrogen- and ammonia-based e-fuels all have an infinite shelf life, in contrast to gasoline and diesel. This is also true for a number of more recent biodiesel and synthetic diesel compositions, which have a 10-year lifespan.

Need For Alternate Fuels

Determining the types of emissions and their sources is important. Fuels including natural gas, gasoline, diesel, fuel oil, mixes of biodiesel, coal, and gasoline all burn when they are burned, releasing exhaust gas or flue gas as a byproduct. Depending on the engine type, it is released into the environment by an exhaust pipe, a flue gas stack, or a propelling nozzle. Realizing the significance of alternate fuel sources is a further key goal. There will come a day when we run out of conventional fuels, like petroleum. Many people worry that since these fuels are often not renewable, there will come a day when there will be a significant global catastrophe as a result of the demand outstripping the supply. Alternative fuels, sometimes referred to as non-conventional and advanced fuels, are any materials or substances that may be used as fuel in lieu of traditional fuels, such as fossil fuels, nuclear fuels manufactured from uranium and thorium, and synthetic radioisotope fuels produced in nuclear reactors. Biodiesel, bioalcohol, refuse-derived fuel, chemically stored power, hydrogen, non-fossil methane, non-fossil natural gas, vegetable oil, propane, and other biomass sources are a few of the more well-known alternative fuels. A study of the benefits and drawbacks of employing alternate fuel sources is required.

1. Traditional fuels will eventually run out
2. Traditional fuels, such as petroleum, will one day no longer be available from our current sources.

Non-environmentalists also share the belief that the bulk of the world's oil reserves, which are mostly located in the Middle East, are linked to issues that are political and economically problematic. This is because these fuels are often not renewable.

The world's reliance on Middle Eastern fuel supplies is causing discontent and violence, thus finding a new approach or solution to the problem of finding other nations to provide new fuels will lessen these effects.

Using alternative fuels significantly reduces emissions that cause ozone to form, as well as damaging exhaust emissions including carbon dioxide, carbon monoxide, particulate matter, and sulphur dioxide.

To combat global warming

According to a widely recognised scientific hypothesis, the use of fossil fuels was raising temperatures in the earth's atmosphere (global warming).

To save money

Alternative fuels have the potential to be more cost-effective than traditional fuels, both in terms of the fuel's overall cost and its longer lifespan. Savings for the future are thus necessary as a result. Waste may be reused Biofuels, bioproducts, and biopower provide the adage that what's garbage to one person may be gold to another a new and contemporary meaning. That's encouraging given that more than 236 million tonnes of garbage are produced in the United States annually.

There are more options

The beautiful thing about alternative fuels and the related cars that operate on them is that there is something to fit every lifestyle. Everybody has his or her own needs, views, and preferences. Why Using biofuels derived from locally grown and processed crops supports farmers' devoted and labor-intensive work. Cooperatives that produce biodiesel and ethanol are the offspring of large, antiquated agricultural cooperatives, which help put power back in the hands of the people.

Since most alternative fuels are produced in-country, there is less reliance on imported energy. Crude oil import costs may be decreased by using locally accessible resources for fuel. The majority of alternative fuels, such alcohols and biodiesel, can be made from biomass resources and agricultural wastes, while power for battery-operated cars may be generated using solar and fuel cells. Gasification of biomass or electrolysis of water may both yield hydrogen. This means that even a tiny fraction of the import of crude oil is reduced by using alternative fuels instead.

The ambient air quality is typically improved by alternative fuels since they lower vehicle exhaust emissions. In contrast to petroleum-based fuels, alternative fuels may lower engine emissions. Alternative fuels' molecules are significantly simpler than those of gasoline and diesel (CH_3OH, C_2H_5OH, and CH_4, among others) (mixture of different molecules). Additionally, alternative fuels that have a low C:H ratio when burned produce less hydrocarbon emissions.

With no hydrocarbon emissions, hydrogen is the cleanest fuel. More readily controllable than vehicle emissions are those coming from centralised plants. When compared to petroleum-based fuels, certain alternative fuels may be more affordable to use. The price is a key factor in the success of any new fuel or product. Most alternative fuels are currently somewhat more expensive than conventional fuel. Compressed natural gas (CNG) and biodiesel are more expensive than petroleum, although they are still reasonably priced. Government incentives and laws are necessary for the development of alternative fuels to some degree. Environmental friendliness: Renewable diesel and biodiesel are also biodegradable, non-toxic, and emit less odours. Similarly, because LPG and natural gas would only evaporate if spilled, none of them is likely to contaminate the land or water. less maintenance requirements Compared to liquid fuels, natural gas and propane typically burn more cleanly. Thus, a less quantity of soot enters the engine's oil. Some operators exploit this by increasing the time between oil changes. This may easily result in savings of $10,000 or more when there is a big fleet of cars involved.

Performance: In addition to having greater cetane and octane ratings than unblended diesel or gasoline, biodiesel and ethanol blends also provide better performance and acceleration. This is one of the reasons NASCAR promotes its usage of a gasoline and ethanol mix in the US that contains 15% ethanol—significantly more ethanol than the typical fuel found at the pump. The use of alternative fuels is far more widespread than most people believe. There are many alternative fuels with a track record that, when used wisely, may assist companies in achieving their environmental and cost-cutting goals.

Alcohols

Energy plays a significant role in the global improvement and advancement of living conditions for people and the sustainability of their growth. The demand for energy in the industrialization and transportation sectors has increased at an even greater rate than the rate at which the world's population has grown over the past few decades, which has directly affected crude oil prices. Crude oil prices are also directly impacted by the strength of the global economy. Today, 58% of all fossil fuels used globally are used exclusively in the transportation sector, which accounts for 80% of all primary energy consumption from fossil fuels. Since 1973, there has been an average annual growth in the primary energy demand of 2.0%. The world's population is still largely reliant on non-commercial fuels, around one third of whom. The extensive use or burning of fossil fuels in several sectors and modes of transportation, which has a negative impact on human health and is a major contributor to air pollution, ozone depletion, global warming, and climate change, is one of the main environmental challenges. CO2, on the other hand, is a significant pollution that is created when fuel is burned improperly, and NO x is another significant pollutant that is created by both natural and artificial processes. Additionally, SO2 is one of the main air pollutants and is created through the burning of combustibles used in manufacturing, such as coal and petroleum.

Alcohols have the potential to transform the supply and use of energy fuels, notably in transportation. This global potential is supported by

(a) the large range of readily accessible raw materials from which alcohols may be produced (coal, natural gas, petroleum, and biomass).

(b) the developed and proven technology for the production and use of alcohol.

(c) The good combustion properties of alcohols, such as clean burning and excellent performance.

Alcohols now cost considerably more than gasoline (which cost approximately $iS/barrel in 1986), which makes them less popular as fuels. Other obstacles include the absence of a distribution network, worries about health protection, and engine issues. Smog in big cities like Mexico City, Los Angeles, and Tokyo City became a significant problem in the 1960s, which helped to draw attention to environmental issues. More than 185 million buses, vehicles, and trucks were utilised in the United States in 1992, according to the National Energy Strategy, using up two thirds of the country's oil supply. In India, for example, transportation used 50% of the country's oil consumption in 1991; by 2010, that number had risen to %. The ecology is seriously harmed by the daily, fast growth in oil use. 1992 saw the Earth Summit on Environment and Development, which was organised by the UN (UNCED). Global warming reduction was the primary goal of this conference for participants from all around the globe.

Consequently, it becomes crucial to look into potential fossil fuel substitutes. In this sense, a replacement that is ideal would be one that uses less-polluting, efficient, cost-effective, renewable, and sustainable energy sources. The most environmentally friendly energy source out of the various energy substitutes is alternative fuels. The world is already discovering one new barrel of oil for every four it uses, according to a disturbing statistical study that shows that global oil and gas production is close to reaching its maximum capacity. Alcohol fuels are the ideal substitute for fossil fuels because they have the potential to boost supply security, cut down on car emissions, and provide farmers with a steady source of income. Alcohol fuels have also been positioned as a future leader in the energy sector. In the majority of the world's nations, alcohol fuel is being utilised as an alternative fuel in various motor vehicles (buses, automobiles, lorries, etc.).

The global ecosystem's future is perhaps the most crucial topic at the moment. Our youthful researchers have recently increased public awareness of environmental protection and the use of alcohol fuels or non-fossil fuels in internal combustion engines. Low molecular weight alcohols, especially ethanol and methanol, make up one class of alternative fuels that are popular for this use. Compared to fossil fuels, alcohol fuel offers the following benefits in greater quantity:

Both of the lower molecular weight alcohols are produced inexpensively and locally from biomass, coal, and natural gas. Due to a larger molal products to reactants ratio when burning alcohol in internal combustion engines (ICE), there are higher combustion pressures than when burning gasoline. Compared to gasoline, this also increases power production and thermal efficiency.

It is possible to minimise emissions of greenhouse gases.

a. Alcohols with higher average octane ratings than gasoline may have more power and fuel economy.
b. Minimizes environmental pollution caused by the release of harmful gases.
c. The spills and leaks of alcohol fuel from oil tankers; as alcohols are miscible with water, they might be quickly and easily removed by washing with water. If absorbed by the earth, they are readily digested and alcohol fuels have fewer evaporative emissions.

Due to alcohol fuel's lower carbon content and insignificant quantity of ash emitted into the environment after combustion in ICE, fuel efficiency might be increased overall.

CHAPTER 14

ALCOHOLS FOR ECONOMIC, ENVIRONMENTAL ISSUES AND SUSTAINABLE DEVELOPMENT

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The supply of commodities or food, the transportation industry, and labour, among other things, depend heavily on oil. Oil reserves are found in a small number of nations throughout the globe, many of which have experienced political and economic instability. Additionally, the oil trade is becoming more volatile and heated between importers and exporters. Alcohol fuel is one of the finest substitutes for fossil fuels as a result. Because alcohol is made from cheap biomass, coal, and natural gas, producing alternative fuels has a far lower cost. As a result, the production of alcohol fuel expands into more territory, making the supply of alcohol fuel less susceptible to interruption. Additionally, the use of alcohol as fuel presents the possibility of a more varied and fairly distributed income source. Alcohol fuel may thus be a more necessary replacement in those nations that rely more heavily on fossil fuels.

Environmental concerns

The harm posed by climate change is significantly reduced when alcohol is used as fuel. Fossil fuels are mostly employed in the transportation sector, which might cause air pollutants such nitrogen oxides (NO x), hydrocarbons, particulate matter, carbon monoxide, and carbon dioxide, among others, to be exhausted. These air pollutants have a significant role in concerns including climate change, greenhouse gas (GHG) emissions, global warming, ozone layer depletion, and difficulties with human health. In order to reduce the need for fossil fuels and the resulting warming emissions from the transportation sector for future generations, it is vital to look for alternatives. One of the finest alternative fuels for the transportation industry to lessen hazardous depletion into the environment is alcohol fuel. Researchers have looked at the consequences of GHG emissions on the vast amounts of natural land that are being converted to farmland across the world to support the growth of alcoholic beverages. The first of these studies, carried out at the University of Minnesota, looked at the carbon debt produced by direct changes in land use when virgin areas are cleared for new crops intended for the manufacture of alcohol fuel.

Sustainable Development

It is crucial to make sure that sustainable development in both the short and long terms is not in contradiction with any country's planning decisions. Each policy must take into account all three of the pillars of sustainable development—social, economic, and environmental. The concept of a clean or healthy environment, priority for social development, satisfaction of economic needs, and the idea that the current generation must not endanger the ability of future generations to be at least as well off as the current generation through damage to ecological processes essential to life are all implied by the term "development." Without sacrificing the potential of future generations to fulfil their own needs, sustainable development satisfies existing requirements. Though it took more than 30 years, the idea of sustainable development began to gain worldwide recognition. Additionally, discussions regarding sustainable development and energy are now receiving considerably greater attention on the global stage.

Energy is essential for sustainable growth and the eradication of poverty. Along with livelihoods, agricultural output, access to water, education, and health, it has an effect on all aspects of development—economic, social, and environmental. Today's population growth throughout the globe raises significant issues. The progress of the economy, from rural economies to modern industrial and service-based civilizations, depends on the availability of enough and appropriate energy. Additionally, energy is crucial to the majority of industrial and commercial wealth creation processes as well as the advancement of social and economic good.

However, the current system of energy production and consumption relies on limited supplies of fossil fuels and is seen to be unsustainable from an environmental standpoint. On the other hand, there isn't any technique for producing or converting energy that is totally risk-free or waste-free. In general, the cycle of energy was began with resource extraction and finished with energy services, pollution, health-related problems, and negative environmental effects. Although a particular technology may not create hazardous elements when it is actually using resources, emissions and waste are constantly connected to its production and other phases of its life cycle. Thus, the circumstance emphasises the need for sustainable alcohol fuels, employing feedstocks that lessen competition for important croplands.

These include waste streams from forests, farms, and municipalities; energy crops grown on marginal areas; and algae. In addition, compared to first generation alcohol fuels like maize ethanol, second generation alcohol fuel feedstock is predicted to dramatically lower GHG. alcohol use as a fuel and sustainable development. In all forms of energy, burning fossil fuels is mostly to blame for air pollution, climatic changes, local acidification, and issues relating to human health. Even while it is acknowledged that governments have the primary duty for sustainable energy policy, success may be aided by a collaborative approach including all parties.

The UN Economic and Social Council (UN ESC) society provided a summary of the essential principles governing the approach to energy for sustainable development. By encouraging technological interchange, the development of capabilities, and financial investments in developing nations, the group of international communities can make the transition from the existing energy system to one that is more sustainable. The seven difficulties listed below were compiled by the UN ESC:

1. Improvements in the use of renewable energy.
2. An increase in energy availability.
3. A rise in energy efficiency.
4. Develop advanced and sophisticated fossil-fuel technology.
5. Development of nuclear energy methods.
6. The improvement of rural energy conditions.
7. Reducing transportation-related emissions and advancing energy efficiency.

ETHANOL BLENDS

Various plant resources generally referred to as "biomass" are used to create ethanol, a sustainable fuel. To oxygenate the fuel and lessen air pollution, ethanol, generally E10 (10% ethanol, 90% gasoline), is added to more than 98% of the gasoline sold in the United States. A flexible fuel car is one that can run on any gasoline and ethanol mix up to an ethanol content of 83%. Ethanol is also available as E85 (or flex fuel), which may be used in flexible fuel vehicles. Model year 2001 and newer light-duty cars are permitted to utilise another mix, E15. 94% of the ethanol used in the United States is made from maize grain starch. For any raw material to become ethanol, energy is needed. Since the energy required to generate ethanol from maize is more than the energy present in the fuel, this kind of ethanol has a positive energy balance.

Because the feedstocks are either waste or byproducts of other industries (such as wood or agricultural residues), or they are specialised crops (like switchgrass and miscanthus), cellulosic ethanol improves the energy balance of ethanol. These crops also need less water and fertiliser than maize. Further reducing the quantity of fossil fuel energy required for production is the use of biomass to power the conversion of non-food based feedstocks into cellulosic ethanol. Cellulosic ethanol also produces less greenhouse gas emissions throughout its life cycle, which is another advantage.It is possible to employ ethanol in a variety of mixtures in both conventional and alternative fuel cars. 10% ethanol and 90% gasoline are used to make the low-level mix E10. The American Environmental Protection Agency (EPA) has given its use in any typical gasoline-powered vehicle its approval. The 1990 Clean Air Act Amendments (and later legislation) required the sale of oxygenated fuels in places with hazardous amounts of carbon monoxide, which sparked the usage of E10. This sparked the establishment of the current ethanol sector in the United States. All 50 states now sell E10. To increase octane, comply with air quality regulations, or fulfil the Renewable Fuel Standard, up to 10% ethanol is used in more than 98% of U.S. gasoline. Under the Energy Policy Act of 1992, E10 is not a recognised alternative fuel (EPAct).

E15

E15 is a light combination of gasoline and ethanol that contains between 10.5% and 15% of ethanol. For use in light-duty conventional vehicles, E15 is allowed for model years 2001 and later. In order to sell E15, stations must abide by a number of EPA guidelines and rules. In order to lessen the possibility of cars older than model year 2001 recharging with E15, it is crucial that a misfueling mitigation strategy be implemented. However, E15 does contribute to meeting the federal Renewable Fuel Standard even if it is not an alternative fuel under EPAct.

E85

The EPAct recognises E85 (also known as flex fuel), an ethanol-gasoline combination that ranges in ethanol content from 51% to 83% depending on the region and the time of year. E85 is compatible with flexible fuel vehicles (FFVs), which have an internal combustion engine and are designed to operate on E85, gasoline, or any gasoline and ethanol mixture up to an 83%

concentration. Approximately 35 different types of FFVs have been created since the 1990s. Since FFVs appear identical to gasoline-only versions, you may use the Alternative Fuel and Advanced Vehicle Search to discover the most recent FFV models or visit Fueleconomy.gov to learn how to distinguish a flex-fuel vehicle from a gasoline-only one. For models that run on gasoline alone, E85 is not authorised for usage.

From Blender Pumps, Intermediate Blends

Fuel from two tanks is drawn and blended by blender pumps, which are dispensers. As an example, a blender pump dispenser may provide three grades of gasoline (regular, premium, and mid-grade) by storing regular and premium in two subterranean tanks. In order to provide mid-grade gasoline, the dispenser may then combine the two. With conventional gasoline and E85 kept in separate tanks, ethanol blender pumps function in the same manner. It gives owners additional possibilities to employ intermediate mixes in FFVs. E85 is only one of several common mixes; others include E25 (25% ethanol, 75% gasoline) and E30 (30% ethanol, 70% gasoline). Fuels for FFVs must be identified on labels in a clear and concise manner. To legally administer E15 to conventional automobiles with model years 2001 and later, blender pumps are also an option.

High-octane fuel (HOF) has the potential to cut energy usage and greenhouse gas emissions. However, there are a number of obstacles standing in the way of its effective market entry, which was the focus of a research supported by the DOE's Bioenergy Technologies Office. The research concentrated on HOF for use in an engine created especially to benefit from the high octane level of the fuel, with an ethanol percentage of 25% to 40%. The possibility of high-octane ethanol fuel is still being researched by business. On the Bioenergy Knowledge Discovery Framework, further information on the HOF research and publications is accessible. The Co-Optimization of Fuels and Engines (Co-Optima) effort is an ongoing, multi-nation laboratory study supported by the DOE that tests high-octane fuels, including ethanol, to increase vehicle economy.

Natural Gas

Undoubtedly, the two fundamental issues in the fight against climate change are energy security and sustainability. A replacement for fossil fuels must be developed, despite the fact that an urgent demand for 100% green and renewable energy seems to be impractical owing to the significant financial costs and weak energy infrastructure. Compared to other fossil fuels like coal, bitumen, and diesel, natural gas, a naturally occurring fossil gas, is a more environmentally friendly energy source. Due to its affordability compared to other fossil fuels like coal and its capacity to facilitate the integration of renewables, natural gas is the greatest option for a sustainable transition to renewable energy in every nation on the planet.

The main component of natural gas, methane, is an odourless, gaseous combination of hydrocarbons (CH_4). It makes up around 30% of the energy used in the US. The remaining fuel is divided between industrial applications, heating and cooking needs in homes and businesses, and generation of electric power, which consumes around 40% of it. Although natural gas has been used for many years to power natural gas cars, only around two tenths of one percent of natural gas is utilised as a transportation fuel. Natural gas is an alternative and sustainable energy source that may be utilised in lieu of conventional fossil fuels (gasoline and diesel). Utilizing natural gas will assist in lowering the quantity of hazardous emissions that are emitted into the environment.

Like conventional fossil fuels, natural gas may be ignited by spark in internal combustion engines but poses no danger to the land, surface water, or groundwater. It is also non-toxic, non-corrosive, and non-carcinogenic.

By using a process known as hydraulic fracturing, natural gas may be produced from gas and oil wells. The majority of applications for natural gas are in manufacturing, industrial processes, and the generation of electric power. Currently, just 1% of the natural gas used is utilised as fuel for transportation. Because it comes from sources created over millions of years by the impact of heat and pressure on biological elements, the great majority of natural gas in the United States is regarded as a fossil fuel. As an alternative, pipeline-quality biomethane, sometimes referred to as renewable natural gas (RNG), is a fuel for vehicles. It is made by purifying biogas, which is created by the anaerobic digestion of organic materials, such as animal waste and landfill trash, or by thermochemical processes, including gasification. The Renewable Fuel Standard recognises RNG as an advanced biofuel. Since RNG is chemically equivalent to traditional natural gas obtained from fossil sources, it may utilise the current natural gas distribution system but needs to be compressed or liquefied for use in cars.

Alternative Fuels for Transportation: CNG and LNG

Currently, compressed natural gas (CNG) and liquefied natural gas are both utilised in cars (LNG). Both products are commercially accessible, made locally, and reasonably priced. According to the Energy Policy Act of 1992, CNG and LNG are regarded as alternative fuels and are marketed in units of gasoline or diesel gallon equivalents (GGEs or DGEs) based on the amount of energy contained in a gallon of gasoline or diesel fuel.

Compressed Natural Gas

Natural gas is compressed to less than 1% of its original volume at ordinary atmospheric pressure to create CNG. CNG is kept inside of a car at a pressure of up to 3,600 pounds per square inch in a compressed gaseous form to offer enough driving range. In light-, medium-, and heavy-duty applications, CNG is employed. On a GGE basis, a car running on CNG achieves almost the same fuel efficiency as a car running on regular gasoline 5.66 pounds of CNG are equated to one GGE.

LNG: Liquid Natural Gas

LNG stands for natural gas in liquid form. Natural gas must first be purified before being rapidly cooled to -260°F to create LNG. The majority of the unwanted chemicals in natural gas are eliminated during the liquefaction process, which involves cooling the fuel below its boiling point. Methane dominates the residual natural gas, with trace levels of other hydrocarbons. The fuel's usage in commercial applications has been constrained due to the comparatively high cost of LNG production and the need to store it in pricey cryogenic tanks. LNG is held in pressure containers with double walls and vacuum insulation at very low temperatures. LNG is appropriate for vehicles that need to go further since liquid is denser than gas and can thus store more energy by volume. Medium- and heavy-duty trucks often utilise LNG. 1.5 litres of LNG are equated to one GGE.

Natural Gas Benefits and Considerations

Natural gas has many benefits as an alternative fuel, including domestic availability, a well-established distribution network, a relatively cheap cost, and reduced emissions, whether it is generated using traditional or renewable techniques. Both conventional and renewable natural gas (RNG) must be compressed (CNG) or liquefied (LNG) before being used in motor vehicles. There are several things to think about while considering the usage of natural gas, just as with any alternative fuel.

Energy Safety

In 2020, the United States became a net exporter of petroleum, with exports outpacing imports, however imports of 7.86 million barrels per day continued to be crucial for maintaining a balance between supply and demand on both local and foreign markets. About 30% of the nation's overall energy demands and 70% of its petroleum consumption are collectively met by the transportation sector. Strengthening national security and lowering transportation energy costs for companies and consumers are two benefits of using natural gas, alternative fuels, and cutting-edge technology to minimise fuel use.

Automotive Performance

Regarding power, acceleration, and cruising speed, natural gas vehicles (NGVs) are comparable to gasoline or diesel cars. Due to the fact that a similar-sized tank of natural gas can only hold so much energy, NGVs often have a shorter driving range than equivalent gasoline and diesel cars. Larger cars' range may be extended by adding additional natural gas storage tanks or using LNG. Dual-fuel, compression-ignited engines are somewhat more fuel-efficient than specialised natural gas engines with spark ignition in heavy-duty vehicles. However, a dual-fuel engine makes the fuel-storage system more complicated since it has to store both kinds of fuel and include diesel aftertreatment equipment.

Decreased emissions

Regardless of fuel source, all new cars must comply with the same emissions rules and are outfitted with efficient pollution control systems. So long as all cars have current pollution controls, natural gas vehicles' tailpipe emissions are equivalent to those of gasoline and diesel vehicles. Light-duty cars powered by conventional natural gas may cut life cycle greenhouse gas emissions by up to 15%, according to the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model from Argonne National Laboratory (reductions are more substantial for vehicles running on RNG). Additionally, the cars don't emit any evaporative pollutants since the CNG fuel systems are totally enclosed.

Renewable natural gas production has other advantages. Renewable natural gas (RNG) is basically biogas, the gaseous byproduct of the breakdown of organic materials, purified by processing. By avoiding the release of methane into the environment, capturing biogas from livestock operations and landfills lowers emissions. As a greenhouse gas, methane outperforms carbon dioxide by a factor of 25. Anaerobic digestion, which generates biogas, also eliminates smells and creates liquid fertiliser that is rich in nutrients.

Access to infrastructure and vehicles

Original equipment manufacturers in the United States provide a range of brand-new, heavy-duty natural gas vehicles. Please refer to the Alternative for availability. Vehicle Advanced Search and fuel. Using certified system retrofitters, fleets and households may also safely convert their current gasoline or diesel cars to run on natural gas. Many automobiles may be converted to run on natural gas in an affordable, secure, and reliable manner by qualified system retrofitters. The National Highway Traffic Safety Administration, the National Fire Protection Agency's NFPA 52 Vehicular Natural Gas Fuel Systems Code, the CSA Group's CSA/ANSI NGV 6.1 code, and state organisations like the California Air Resources Board all have emissions and safety standards that all vehicles and engine conversions must adhere to.

The infrastructure for fuelling vehicles is sparse in the United States, despite its massive natural gas distribution network. Due to this, a lot of fleets either decide to invest in their own, often expensive, natural gas fuelling infrastructure or work with other fleets to create a shared infrastructure. This kind of infrastructure partnership has various advantages, including a shorter payback time and increased throughput, which often translates to cheaper fuel costs.

Around 23 million automobiles globally and more than 175,000 in the United States are powered by natural gas. Because they may accommodate applications that remain within an area with consistent CNG fuelling, natural gas vehicles (NGVs) are attractive options for high-mileage, centrally fuelled fleets. For long-distance automobiles, liquefied natural gas (LNG) has a higher energy density than compressed natural gas (CNG), resulting in a fuel range that is more equivalent to regular gasoline. Natural gas is superior to traditional gasoline and diesel fuels for use as a transportation fuel since it is domestically available, has a large distribution network, and emits less greenhouse gases.

Biogas

As a "greener" fuel, biogas has grown in popularity in recent years. This methane, which may be used to replace traditional natural gas, is produced when anaerobic digestion breaks down organic matter, such as in landfills or "digesters" that transform animal manure or food waste. But can you really call it a renewable energy source? You won't be shocked to learn that it's difficult, I suppose. Biogas is unquestionably a more environmentally friendly choice when compared to virgin natural gas that is extracted by drilling into the soil. In order to fracture rock formations, water, chemicals, and sand are injected deeply into the earth during the fracking process, which accounts for around 80% of the extraction of natural gas in the United States. Landscapes and ecosystems may sustain substantial harm from the fracking process. By using material that already exists and would otherwise go to trash, landfills and digesters provide a comparable fuel without harming the environment like fracking does.

Biogas also has other advantages. Nitrogen pollution and discharge into water resources are prevented by removing the environment's large supply of animal manure and food waste. Additionally, methane emissions from landfills and manure lagoons that would have otherwise leaked are reduced by the use of biogas. By turning this methane into CO2, which has a global warming potential of up to 34 times less than methane, using it as fuel significantly lessens its influence on the climate.

In lieu of coal or natural gas, stored biogas may provide a safe, dependable, and sustainable source of baseload electricity. To fulfil minimal power requirements, baseload power is continuously generated; renewable baseload electricity may support more intermittent renewables. Biogas may be utilised as a source of peak power that can be quickly scaled up, much as natural gas can. Utilizing stored biogas reduces reliance on fossil fuels and restricts the quantity of methane emitted into the atmosphere. By using all of the possible biogas in the United States, methane emissions would be reduced by 800,000 to 11 million passenger cars' worth of emissions annually. According to a waste-to-wheels analysis, compressed natural gas made from biogas decreases greenhouse gas emissions in comparison to petroleum fuel by up to 91%.

Anaerobic digestion has advantages for the environment in addition to lowering waste cleanup costs and boosting regional economy. Over 335,000 temporary construction employment and 23,000 permanent jobs might be generated by the building of the 13,500 possible biogas systems in the US. Additionally, anaerobic digestion lessens infections, smells, and the possibility of animal waste polluting water sources. Digestate, the substance left behind after digestion, may be utilised as fertiliser or sold, lessening the need for artificial fertilisers. When marketed as a soil conditioner or as bedding for animals, digestate may provide extra income.

The correct processing can enhance biogas such that it may take the place of mined natural gas as a fuel for power generation, ground transportation, and the construction of both commercial and residential structures. However, in general, we can and should electrify as many end uses as we can, including buildings and ground transportation, by using zero-carbon energy sources like wind and solar to produce electricity.

Several significant industrial processes that produce the items we need, including those that produce steel, cement, food, and consumer goods, required very high heat, which is now only available from gas. There is really no way to a 1.5C future without tackling these emissions, which account for more US carbon than the agriculture sector (11% on average). Biogas may be a part of the answer since it is anticipated that this industry will continue to consume natural gas for many years to come. But to do this, the US must significantly increase the quantity of biogas collected.

In order to achieve precisely that, WWF's Renewable Thermal Collaborative (RTC) was established. The RTC today consists of over a dozen influential commercial and industrial buyers and sellers of renewable technologies committed to working together to find a solution to the thermal problem. Together, we are attempting to remove the many technological, commercial, and regulatory obstacles that prevent biogas and other technologies from becoming widely accessible and cost-competitive with fossil fuels.

In the sense that people and animals will continue to produce waste, biogas, also known as renewable natural gas, is "renewable"; nonetheless, we do not wish to promote the production of further trash for the express purpose of producing additional biogas. After all, burning the gas still has an effect on the environment, even if collecting and utilising methane is preferable than letting it escape to the sky. By collecting and storing the CO2 produced during the burning of the biogas, we may further lessen this effect, but this is just a partial solution since there are hazards involved.

Ultimately, even if biogas is now a more environmentally friendly alternative to conventional natural gas, we should still see it as a crucial transition fuel on the way to fully decarbonizing our energy supply.

CHAPTER 15

ALTERNATE FUEL SOURCES

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Alternative fuel vehicles (AFVs) are simply cars that operate on fuels other than regular gasoline or diesel. The definition of what actually qualifies as an alternative fuel vehicle (AFV) varies slightly depending on the context and who is setting the parameters, but there are numerous fuel types, and combinations of fuel types, that would qualify a car using them to fall under the alternative fuel vehicle category. Everything you need to know about alternative fuel vehicles will be covered in this tutorial.

However, some of these alternative fuels are well-liked in other markets around the globe, and biofuels are present in small amounts as an additive in all UK gasoline and diesel. It is important to note that none of these alternative fuels have had a significant impact on the UK automobile market as of yet. Of fact, one alternative fuel, electricity, is now revolutionising the worldwide auto industry in front of our own eyes.

Hydrogen

Fuel cell electric cars are powered by hydrogen, which is readily available in our environment and is found in water, hydrocarbons, and other organic stuff (FCEVs). The attractiveness of FCEVs is based on their effectiveness, quick filling times, and most importantly, their emissions of only warm water. But since extracting hydrogen particles is a laborious procedure, hydrogen has a lower energy content than gasoline or diesel. FCEVs still haven't made it to the mainstream market, in part due of this manufacturing bottleneck. Creating a sizable fueling infrastructure might be expensive and challenging, but that doesn't imply it isn't doable. In fact, LGM is pleased to be a sponsor of the first retail hydrogen station in Canada, which opens this month in Vancouver. As a consequence of the collaboration between Shell Canada and HTEC (Hydrogen Technology & Energy Corporation), the station will be the first in a network of six stations. Read the notice we posted in March for further details.

Electrical

Electricity is a very effective energy source that is easily accessible to us because to a built infrastructure. It is derived directly from the electrical grid and other off-board electric power sources. All-electric and plug-in hybrid electric vehicles (PHEVs) run on electricity stored in their rechargeable batteries, which produce a lot less pollutants than cars or trucks with internal combustion or diesel engines.

Electricity takes the role of gasoline in gas-electric hybrids while travelling at lower speeds and during acceleration and deceleration. Similar to EVs, PHEVs utilise energy to power the vehicle over longer distances while emitting no emissions when the vehicle is powered only by its battery. Although the cost of fuel for electricity may be cheaper, the cost of an actual electric vehicle (EV) might be much more than that of a typical gasoline-powered automobile. Additionally, a significant portion of today's power is generated by burning coal or natural gas, which raises questions about how much carbon is emitted overall.

Biodiesel

Biodiesel is apart from normal petroleum diesel, as we are all familiar with it. It is a renewable, extraordinarily clean-burning byproduct of non-toxic, biodegradable materials including recycled restaurant grease, animal fats, and vegetable oils. B5 is a combination of 5% biodiesel and 95% regular diesel, for example. Pure biodiesel is also available (B100). Although biodiesel-powered cars do release carbon dioxide (CO2), they do so less than all-electric zero emissions vehicles, so there is some good news. It is a greener alternative to gasoline or diesel since any CO2 emissions are balanced by the CO2 absorbed by the feedstock crops used to make biodiesel (such as soybeans).

Because of its low output and lack of a distribution network, biodiesel, especially in its pure form, may be more expensive than regular diesel. However, this depends on the market and the locality. Additionally, since biodiesel has 10% less energy than regular diesel, it requires more gasoline to run a vehicle fueled by it.

Ethanol

Consider crops like maize, barley, and wheat as the renewable ingredients used to make ethanol, an alcohol-based fuel. Today, a number of ethanol mixes are employed, although E10 is the most popular (10% ethanol and 90% gasoline). Other mixes include E85, a "flex fuel," which is used in cars that can run on gasoline alone or a combination of up to 85% ethanol and 15% gasoline. E15 is used in models made in 2001 and after.

Similar to biodiesel, ethanol is produced using crops that reduce the amount of CO2 released during burning. Ethanol can thus increase our energy security and air quality by lowering the quantity of pollutants that are released into the environment. But ethanol production requires a lot of energy. Resources are used up in the process, which has an adverse effect on food costs and availability and creates additional potential for CO2 emissions. A vehicle would normally get less miles per gallon of ethanol than it would if it were fueled entirely by gasoline due to the difference in energy content between the two, which affects fuel economy (the ratio of the distance travelled to the amount of fuel used by a vehicle.

Propane

Propane, commonly referred to as liquefied petroleum gas, is a byproduct of the processing of natural gas and the refining of crude oil. It is similar to a colourless liquid while it is kept, turning into a gas only when burned. We utilise propane gas in our houses and water heating systems, refrigerators, and to power industrial equipment. Like electricity, propane is domestically accessible via a well-established infrastructure constructed around consumption, transportation, storage, and distribution. Its clean burning characteristics make it a viable alternative fuel source since they pose no risk to soil, surface water, or groundwater. The composition's high energy density and comparatively cheap fuel cost make it more alluring. Although propane is a cost-effective fuel, cars driven by it may be more costly than EVs. In addition, like natural gas, propane contributes to methane emissions despite having a lower carbon concentration than gasoline or diesel.

Benefits Of Alternate Fuel Vehicles

There are thousands of cars using fuel substitutes for traditional gasoline and diesel on American roadways, and more are being added every day. Among these alternative fuels are compressed natural gas (CNG), liquified natural gas (LNG), liquid propane gas (LPG), methanol (M85), ethanol (E85), biodiesel, electricity, hydrogen, and fuels made from biological materials. Alternative fuel vehicles (AFVs) are being added to fleets for what reasons? The general population and fleet operators may both profit.

Positive Effects of Alternative Fuel Vehicles

Air Quality Benefits

Compared to gasoline and diesel vehicles, AFVs emit less emissions and harmful pollutants. Comparing alternative fuel cars to those powered by gasoline and diesel, the hazardous emissions from these latter two are fundamentally lower. Particularly large reductions are made in start and evaporative emissions. Alternative fuel cars as a consequence lessen their negative effects on human health, the environment, global warming, and air quality. Utilizing alternative fuel cars is essential for South Carolina's environment and public health since the transportation industry is the fastest-growing source of hazardous pollutant.

Fiscal Advantages

Depending on the fleet, the kind of vehicle being considered, and other site-specific criteria, AFVs may or may not provide particular economic advantages. While the initial cost of buying or converting cars to run on alternative fuels is still greater than it is for cars that run on petrol or diesel, the cost of fuel and maintenance may be cheaper over the course of the car's lifetime. lessen reliance on foreign oil imports. Alternative fuels may be harvested and manufactured locally, lessening our reliance on a limited supply of imported oil that is prone to price and supply swings. Additionally, the market for alternative fuels and the development of domestic energy sources support the expansion of the domestic economy.

Fuel that can be replenished

In order to create fuels more efficiently and lessen reliance on limited energy sources, several alternative fuels are made from renewable sources of energy. Corn and other grains or biomass with a high starch content, for instance, may be fermented to produce ethanol. After processing vegetable oils, biodiesel is produced. A near limitless supply of raw materials may also be used to produce ethanol and biodiesel, reducing waste.

Laws and Regulations

The National Energy Policy Act mandates that alternative fuel vehicles (AFVs) be included in the fleet acquisitions of the federal, state, and alternative fuel provider governments. The US Department of Energy (DOE) opted against requiring fleets operated by local governments and the general public to buy AFVs. The DOE intends to look into alternatives to the private and local regulation, such as swapping alternative fuel consumption for credits toward an AFV purchase and credits for buying medium- and heavy-duty AFVs. less danger from spills. In comparison to gasoline and diesel, alternative fuels often provide advantages for safety and the environment. In the unusual case of a leak, for instance, natural gas would dissipate fast since it is lighter than air. Consequently, unlike spills of gasoline and diesel or leaky underground storage tanks, any prospective leaks of natural gas won't harm the land and water. Because natural gas has a greater ignition point than petroleum-based fuels, the danger of combustion is also reduced. Another example of a substance with a lower spill risk is biodiesel (B100), which is harmless and biodegradable. As opposed to gasoline and diesel fuels, plain biodiesel (B100) does not carry the same risks for contaminating land and water if it is spilled. "Green" living Not to be understated are the advantages of goodwill. A company's dedication to environmental stewardship is clearly shown by its use of alternative fuel cars.

Downsides

The biggest disadvantage is that cars often can't be refuelled at the local gas station. Many alternative fuels just recently began to have the infrastructure needed to fuel them. In order to avoid this, utilising AFVs in fleets rather than privately owned vehicles is now promoted.

Because they regularly travel routes where the gasoline is available or return to a certain spot to refuel, fleet vehicles are suitable candidates. A smart first step would be to purchase a car that can run on either conventional fuels like gasoline or diesel or an alternative fuel. The need for alternative fuels should increase due to fleet usage soon, making them as accessible as gasoline or as near as your home's electricity or natural gas supply. You will quicken that process if you become involved in the movement toward alternative fuels right now. For your fleet right now, are alternative fuels feasible? Undoubtedly, you must come to your own conclusion on the issue. Alternative fuel cars, however, as well as their fuels, are already available.

Future Of Alternate Fuels

Every aspect of our lives involves the usage of energy, thus it is crucial for us as instructors to educate our pupils about the current types of energy we use as well as the new ones that are emerging. Since non-renewable energy sources are depleting rapidly, it is essential for kids to learn about renewable energy sources now so they will be better prepared and more conscientious consumers of energy resources as they become older.

The most widely utilised fuel is gasoline, which is used for transportation. However, a variety of substitute fuels are also entering the market. Propane, natural gas, electric hybrids, hydrogen fuel cells, and biodiesel are just a few examples of these alternative fuels. Most students have heard of some of these alternative fuels, but they may not be aware of how and why they are superior to regular gasoline. The assignments in this area are intended to provide students the chance to do their own research on alternative fuels and how they relate to transportation, as well as to test those theories.

The vehicle industry's future is in the hands of alternatives. Both in terms of improved performance and lowered health risks, there is a lot of promise. However, there hasn't been any genuine interest in alternative fuels from the automotive industry. Take into account the fact that switching to alternative fuels may cut your chance of developing cancer by up to 90%. They need less upkeep and are much more fuel-efficient. However, fewer than 1% of automobiles are powered by alternative fuels. There are several substitutes available today, including electricity, solar energy, biodiesel, liquefied petroleum gas (LPG), methanol, and hydrogen fuels. There are several benefits as well:

CNG and LPG are the two kinds of natural gas, both of which are present in the gaseous state at standard pressure and temperature. CNG significantly reduces pollution without sacrificing performance compared to diesel and gasoline. In comparison to a car with a diesel or gasoline engine, a cng vehicle's co2 emission level is around 40% lower. Considering that the gasoline is devoid of lead and sulphur, even those emissions are eradicated. To develop a cleaner and more sustainable energy system, a replacement for fossil fuels is becoming more and more necessary. The most desirable clean energy solution combines alternative fuel with renewable energy.

Adoption of alternative fuels is motivated by the potential to lower energy costs, lessen reliance on crude oil, increase energy mix diversity, and lower emissions from the extraction and burning of fossil fuels. Modern biomass conversion methods make it possible to turn cellulose and hemicellulose, two substances that are difficult to extract from biomass feedstocks, into fuels that are suitable for transportation. The production of alternative fuels will not be revolutionary; rather, it will be evolutionary, using as much of the infrastructure of the fuel market as possible. The emergence of vehicles using alternative fuels is now underway, but one of the obstacles is that the infrastructure for refuelling may not yet be in place to support its expansion. Therefore, the expansion of the alternative fuel industry is dependent on infrastructure development, which is a necessary but inadequate requirement.

Because of economies of scale, alternative fuels are distinguished by their stable or decreasing fuel costs. The availability, geography, and feedstock processing of biomass have a big impact on how much alternative fuels cost. Finding more productive energy crops and affordable materials for the manufacture of alternative fuels, as well as developing more effective conversion technologies, would significantly lower the cost of producing alternative fuels and improve their competitiveness against fossil fuels. The creation of a low-carbon economy is facilitated by the promotion of technological ideas such as waste-to-energy, power-to-X, and X-to-liquid. The fulfilment of "zero emission" and "zero waste" goals will be aided by alternative fuel generation. Cars will become low-pollutant, and alternative fuel will make cities carbon neutral. Additionally, food and agricultural waste may be converted into alternative fuel, helping to reduce the amount of garbage that ends up in landfills.

1. The research clearly demonstrates the following:

2. Overview of present developments in the generation of alternative fuels
3. The variables influencing the development and use of alternative fuels; • The essential characteristics, shortcomings, significant developments, and research and development (R&D) activities

Technology benchmarking for wise judgements, SWOT analysis, and a snapshot of biofuels and hydrogen production technologies, applications, and future prospects. Researchers and automakers will go on refining and developing the transportation technology we've described. They are investigating more effective uses of alternative fuels, fuel cells, and EV and HEV systems. In order to build cars that operate cleaner and use less gasoline, researchers are also researching on novel energy storage methods and developing lightweight innovative materials. In addition to the current technologies, researchers all over the United States are creating brand-new, cutting-edge technologies for use in cars, minivans, pickup trucks, sport utility vehicles, buses, and heavy-duty trucks that will help us move toward an even cleaner future with more readily accessible, domestic fuel sources.
