Fuels and Energy

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By

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PREFACE

Human civilisation grew up with the application of fire produced from biomass. Burning is an oxidation reaction of any material that liberates energy. The material can be combusted until it reaches the highest oxidation state. Starting from forest burns to the recent advancement of nuclear fuels, there were stages of development. Types and classification of the fuels upstream and downstream processing of the fuels (biomass, petroleum, coal, natural gas, nuclear fuels, hydrogen, fuel cell and alternative liquid fuels) quality control and combustion technology for energy extraction, recent advances in the field and scope of research and development in fuels and the energy sector and sustainability are some of the thrust areas to be addressed. Considering the recent trends of emission from the energy industry, stubble burning of agro-residue, accidental forest firing and emissions from the transportation sector, the mechanism of the actual combustion process is required to be implanted to the upcoming readers. What different advanced formulations from the coal, petroleum and alternative fuel fractions can be formulated for the existing combustion systems for power generation and transportation, without compromising the efficiency and recent emission protocols are promising research areas. This book envisages addressing all the issues starting from the classification of fuels for energy production and utilization, highlighting the prospect of future research in this arena. As a researcher and teaching professionals, we need a comprehensive book with basics that summarizes all the issues together.

This book covers the broad spectrum of classification of fuels, techniques used in upstream processing and downstream processing of fossil fuels, quality control, combustion and emission characteristics of fuels, stoichiometry and actual combustion, hydrogen, fuel cell and new formulation and recent advances in the field of fuels and energy. It has 17 chapters including the most relevant aspects of Fuels and Energy. The uniqueness of each chapter is abstracted under learning outcomes, followed by actual contents briefing.

This book promises to offer a comprehensive book for teaching and research from undergraduate to postgraduate students and start-up faculties. We expect that the contents will fulfil the rising demand for a comprehensive book on the subject from the readers. We also promise that we will be readily accessible for updating the contents of this book if the demand increases from the readers.

The authors acknowledge the moral support received from their respective family members, colleagues, teachers and friends during the preparation of this manuscript.

Dr Sarma acknowledges especially to his wife Mrs Karabi, and Sons, Nishant and Divyansh for their moral boost during this critical period. He admires all the help he received from the teachers during different stages of his education since childhood as he grew up in an economically weaker family. He is also thankful to the authorities of his current Institute for facilitating his desires as authors and researcher.

Thank you for embarking on this journey through the world of fuel and energy. Together, let us explore the dynamic world of fuel and energy, and strive towards a sustainable and prosperous future for all. We expect ample love and respect for this book from the esteemed readers.

Anil Kumar Sarma and Uplabdhi Tyagi

CHAPTER 1

DEFINITION AND CLASSIFICATION OF FUELS

Learning Outcome

The learning outcomes of understanding the definition and classification of fuels can be articulated as follows:

1. Understanding the Concept of Fuels

- ***Definition of Fuels**: Grasp the fundamental definition of fuels as substances that produce energy through combustion or nuclear reactions.*
- ***Energy Production**: Comprehend how fuels release energy, which can be harnessed for various applications, such as heating, electricity generation, and transportation.*

2. Categorization of Fuels

- ***Primary vs. Secondary Fuels**: Differentiate between primary fuels (natural and unprocessed, e.g., coal, crude oil, natural gas) and secondary fuels (processed from primary fuels, e.g., gasoline, diesel).*
- ***Renewable vs. Non-renewable Fuels**: Classify fuels based on their renewability:*
  - ***Renewable Fuels**: Understand examples like biofuels, hydrogen, and their sustainable nature.*
  - ***Non-renewable Fuels**: Recognize examples like coal, petroleum, natural gas, and their finite nature.*

3. Types of Fuels and Their Characteristics

- ***Solid Fuels**: Learn about solid fuels such as coal, wood, and biomass, including their properties, advantages, and disadvantages.*
- ***Liquid Fuels**: Understand liquid fuels like petroleum products (gasoline, diesel), ethanol, and biodiesel, focusing on their characteristics and uses.*
- ***Gaseous Fuels**: Explore gaseous fuels such as natural gas, propane, and hydrogen, including their storage, handling, and applications.*

4. Environmental and Economic Impacts

- ***Environmental Impact****: Assess the environmental implications of different fuels, such as greenhouse gas emissions, pollution, and ecological disruption.*
- ***Economic Impact****: Evaluate the economic aspects, including the cost of extraction, production, and the market dynamics of different fuel types.*

5. Technological and Practical Applications

- ***Technological Uses****: Identify the various technological applications of different fuels in sectors like power generation, transportation, and industry.*
- ***Practical Considerations****: Understand practical aspects such as the efficiency, energy density, and logistical considerations of different fuel types.*

6. Future Trends and Innovations

- ***Emerging Technologies****: Explore new technologies and innovations in fuel development, such as synthetic fuels, fuel cells, and advancements in renewable energy sources.*
- ***Sustainable Practices****: Recognize the importance of sustainable practices and the transition towards cleaner and more efficient fuels.*

By achieving these learning outcomes, students will gain a comprehensive understanding of the definition and classification of fuels, enabling them to make informed decisions and contribute to discussions on energy production and consumption.

1.0 What is fuel?

It is believed that early human beings *Homo erectus* had discovered the fire. Fire is the actual visible energy that initiates burning. A material that releases energy in the form of heat, light or electricity on reacting with another substance (i. e. burning) is called **fuel**. The energy released from the fuel is used for useful work. A fuel is a substance burned to produce heat or power. Initially, the concept of fuels to energy was used solely for those materials capable of releasing chemical energy. Merely with the progress of science and engineering, the concept was extended and applied to many other sources viz. heat energy, nuclear energy, fuel cell electricity, cellular energy etc. A typical fuel (in the form of compounds) contains carbon, hydrogen and sulfur as combustible elements along with nitrogen and other metallic or nonmetallic elements as incombustible components. Sulfur, nitrogen and inorganic constituents are undesirable components of fossil fuels from environmental and ecological perspectives.

1.1 Classification of Fuels

Fuels are broadly classified concerning their occurrences as: 1. **Naturally occurring fuel (or Primary fuel)** viz. biomass, coal, peat, crude oil, natural gas, uranium etc. which are formed from the remains of ancient plants and animals 2. **Synthetic or derived fuels (Secondary fuel)** viz. coke, gasoline, ATF, kerosene, diesel, biodiesel, ethanol, gasohol, butanol, green diesel, dimethyl ether, LPG, LNG etc which can be used as a substitute for oil or natural gas. It is to be remembered that primary fuels are mostly used for power generation purposes via direct combustion route while secondary fuels are derived as compatible from primary fuels for transportation and used for **clean combustion purposes**.

Fuels are sometimes classified as **fossil fuels** (made of organic residue) viz. coal, peat, crude oil, natural gas etc.; **non-fossil fuels** viz. biomass, biofuel, biogas, producer gas etc.; **nuclear fuels,** viz, uranium, thorium, hydrogen etc.

Fuels are classified based on their state of existence at normal temperature and pressure (NTP) as **Solid, Liquid** and **Gaseous fuels**. **Solid fuels** refer to different forms of solid material that can be burnt to release required energy, providing heat and light through the process of combustion. Solid fuels include biomass, coal, coke, charcoal, synthetic fuels, nuclear fissile materials etc. **Liquid fuels** are combustible or energy-generating molecules that can be harnessed to create different forms of mechanical energy, usually for the production of kinetic energy. Liquid fuels include crude oil and distillates (gasoline, kerosene, ATF, diesel), biofuel (biodiesel, green diesel, ethanol, emulsion, dimethyl ether etc.), coal tar (liquified coal) and distillates, synthetic liquid fuels (dimethyl ether produced from natural gas), liquified petroleum and natural gas (LPG, LNG) etc. Whereas gaseous fuel means a material that is in the gaseous state at standard atmospheric temperature and pressure conditions and that is combusted to produce heat and/or energy. G**aseous fuels** are natural gas, refinery gas, biogas, producer gas, water gas, coal gas, hydrogen etc.

Fuels are also classified based on their hazardous fire extinction purposes. Four such categories of classifications are often used: **Class A**: wood, paper, trash, plastic and all other solid combustible material other than metal; **Class B**: flammable liquids such as gasoline, kerosene, oil, grease, acetone, alcohol and all combustible materials in liquid form; **Class C**: energized electrical equipment that causes fire; **Class D**: potassium, sodium, aluminum, magnesium etc. Individual fossil fuels are classified based on their fuel qualities and composition.

1.2 Origin of coal

Coal accounts for the highest energy generation (37% power generation) in the world. Coal is found throughout the world just under the ground in between 55-460 m depth. It is presumed that coal formation began in the carboniferous period, also called the first coal age, and during 369-290 million years ago. *Archaeopteris,* the dominant tree species available during that period were devasted due to ecological reasons. At various stages of geological development, the earth's interior was very hot during that period, while the earth's crust was suitable for *flora and fauna*. As stated by scientists, the dense forests in low and wetland areas were destroyed due to ecological evolution and natural calamities. Subsequent, floods, earthquakes or tectonic movement of the earth system buried those biomasses. As more and more soils were deposited over them, they were compressed. The temperature at the deeper of the earth was also higher while biodegradation and oxygenation of these masses were prevented by mud, acidic or saline water. Under the mud and soil, those trapped carbon-rich biomass were later converted to peat bogs with age. With time, under sedimentary pressure and due to further volcanic or tectonic displacement, the peat bogs were converted to coal at high temperatures and pressure. The organic and biomass origin of coal can be ascertained from their composition, fossil deposition and comparison with present-day biomass.

Coal is classified based on archaeological data, composition and characteristics as, **Anthracite, Bituminous and Lignite**. Anthracite is the oldest, hardest and highest carbon-containing coal, while, lignite is the softest and lowest carbon-containing coal. Coals are further classified as semi-anthracite, semi-bituminous and sub-bituminous etc. The details of the composition of coal are presented in **Table 1.1**, based on some qualitative and quantitative properties. Sometimes coal is classified based on sulfur contents viz. high sulfur and low sulfur coal. Sulphur content in coal varies with different geographic locations and from reserve to reserve. Sulphur may present as inorganic (pyrites or another metal sulphide) and organic (heterocycles). A volumetric research work is available for Sulphur removal which is the most undesirable component of coal (Calkins, 1994).

Table 1.1 Composition of coal from Germany, India and World average.

Detail composition	German Coal	Indian coal	World average
Ash content (%)	6-8	40-50	1-16
Sulphur (%)	0.3 -1	0.5	0.3- 1.8
Carbon (%)	50-57	25-30	53-57
Hydrogen (%)	3.75-6	<3	4-6%
Oxygen (%)	2.5-34	30-40	20-40
Calorific value (Kcal/kg)	6804- 8436	2450-3000	5000-6400

Based on the ratio of hydrogen: carbon and oxygen: carbon in a two-dimensional plot, coal can be classified and linked to its maturity of formation, initially developed by Prof Dirk Willem van Krevelen (1914-2001), commonly known as the van Krevelen diagram. This diagram also proves the hypothesis that the coal is of biomass origin. A typical van Krevelen diagram to link the biological origin of coal is depicted in **Fig. 1.1**. The coal having the highest carbon (%) and lowest oxygen (%) falls near the Y axis, while away from the Y axis and tends towards the X axis means increased of oxygen (%) and decrease in carbon (%).

Stanley (2016) made a different approach to the classification of coal concerning increased carbon % (Y-axis) and decreased Calorific Value (BtU) in the X-axis, as shown in **Fig. 1.2**. This classification is found to be very useful for the different utility of the coal in the United States.

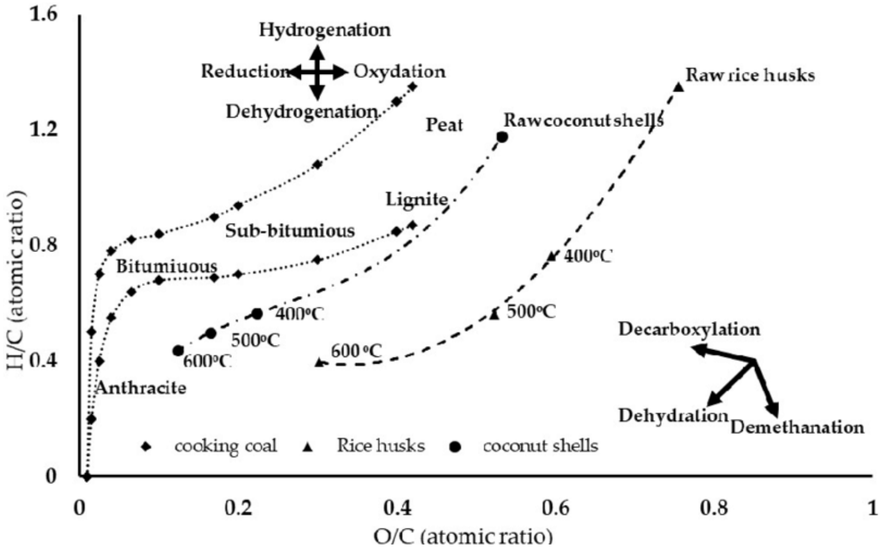

Fig. 1.1. Van Krevelen diagram for classification of Coal.

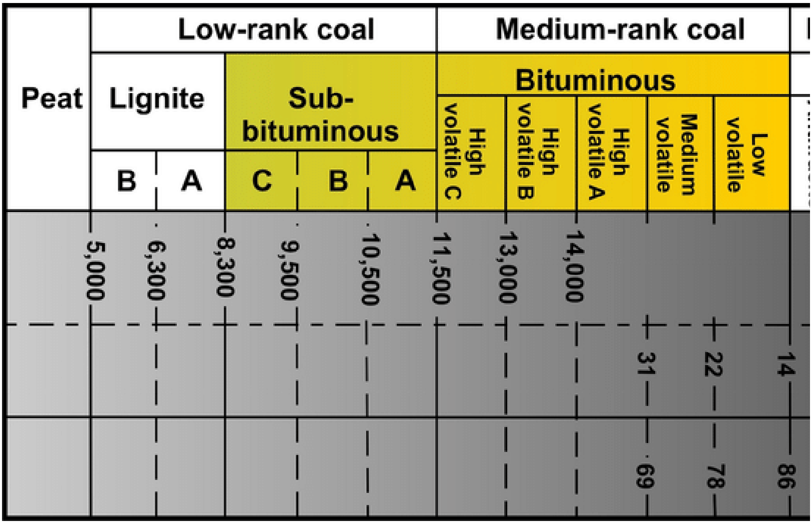

Fig. 1.2. Classification of coal by rank in US (Modified from, source, Stanley P. Schweinfurth - "An introduction to coal quality", US Geological Survey, Professional Paper 1625-F)

Coal is also classified as **coking, non-coking and caking coals** based on their transformation on heating. One of the most important properties of matured coal is the formation of a hard mass called coke when heated in the absence of air. Coke is porous, thermosetting (i.e. cannot be melted to liquid), produces high heat and can support the massive load of a blast furnace charge. Thus, it is very much suitable for blast furnace operation and can be used for steel making. Coal that forms good quality coke is called **Coking** coal. **Non-coking coal,** on the other hand, is less matured and sub-optimal in constituents, with varying percentages of carbon and a significant amount of oxygen and hydrogen present in it. This does not form a similar hard mass when heated, but forms powder char and is therefore used in thermal power plants for direct combustion purposes. This coal can also be useful for liquefaction to be discussed in the succeeding chapters. Coal can also be classified based on its transformation effectiveness for liquefaction which will be discussed in the subsequent chapters. Australia, Germany, the USA, China etc. have high-quality anthracite coal, while India has major coal reserves (2.8×10^5 MT) that include bituminous, subbituminous and lignite only.

Caking coal is an intermediate matured stage coal, with a significant amount of oxygen present in its composition. It melts when heated but does not form a strong coke which can be used in blast furnaces. Thus, it can be stated that all coking coals are caking, but all caking coals are not suitable as coking coals. Sulphur content in coal varies with different geographic locations and from reserve to reserve. Sulphur may present as inorganic (pyrites or another metal sulphide) and organic (heterocyclic compounds). A volumetric research work is available for Sulphur removal which is the most undesirable component of coal (Calkins, 1994).

1.3 Classification of Petroleum Crude Oil

Crude oil accounts for more than 80% of requirements in the transportation sector in the form of distillates in liquid form (gasoline, ATF, diesel, fuel oil) whereas, only 4% for power generation. Crude oil is a mixture of hydrocarbons, aliphatic, aromatic with or without heteroatom ranging from C 4 to C 24 or higher in their carbon chain with many other minerals available on the earth and usually found in thick liquid form. The general composition of petroleum crude oil is presented in **Table 1. 2**.

Table 1.2 Average Crude oil Composition (in the world)

Composition	% by mass	Types of compounds
Carbon Hydrogen	84 14	Aliphatic (straight, branched or cyclic) and aromatic hydrocarbons.
Oxygen	1	Organic acid and heterocyclic compound
Sulfur	1-3	Mercaptans and heterocyclic compounds
Nitrogen	1	Porphyrin, amino acids (aliphatic or aromatic)
Mineral & Salts	0.1	Silica and metallic minerals above 20 traceable metals that affect distillation process

1.3.1 Origin of petroleum

Petroleum crude oil is a yellowish-to-black liquid formed several million years back under the earth, as foretold. As stated by experts only little is known about the earth's interior as compared to the vast astronomic knowledge of the scientific community, and the same is also true for the formation of crude oil. Crude oil is not a uniform substance and its characteristics and appearances vary widely from well to well in the same oilfield. Besides having a varied composition of hydrocarbons, it contains dissolved solids, gases and colloidal suspension. Institute of Petroleum (IP) methods defines crude oil as “A naturally occurring mixture containing predominantly of hydrocarbons and/or of S, N and/or oxygen derivatives of hydrocarbons which is removed from the earth in the liquid state or is capable of being removed” (ASTM D88). Two theories are prevalent for the formation of crude oil, viz. Bionic (Organic) theory and Abionic (Inorganic) theory.

The organic theory proposes that crude oil was formed similarly to coal from the residual mass of organisms other than trees. The organism might include algae, plankton and lower microorganisms that grown by sunlight deep within the sea. The carbon-hydrogen and organic matter relationship is the primary basis of this theory. Porphyrin and nitrogen compounds are present in crude oil and also support the biological origin of petroleum crude oil. The petroleum reserves are most commonly located near the sedimentary basin also supports this theory. Porphyrin is oxidizable if in contact with oxygen and a temperature above 200 ^{0}C. Thus, there is a strong belief that the sedimentary basin never exceeds temperature beyond this and is also supported by geological data. The organic theory became the accepted theory at the turn of the century as the oil and gas industry began to fully develop and geologists were exploring new deposits. Simply stated, the organic theory holds that the carbon and hydrogen necessary for the formation of oil and gas were derived from early marine life forms living on the Earth during the geologic past primarily marine plankton, buried under the earth and sedimented. The carbon, and hydrogen portion was converted to petroleum and gas while the rest of the sedimentary rock was in the usual geological processes. The liquid and gases migrate through the porous rock structure with time due to pressure and flowability or may by tectonic processes till an immovable rock structure(reservoir) is found. Plankton (Phytoplankton, Zooplankton) create the oil by synthesizing fatty acids. Fatty acids are essential constituents of animal fats and animal and plant oils. The general formula for these acids is C_nH_{2n} + 2COOH or $C_nH_{2n}O_2$ and they form the largest known source of long-chain molecules. This is important because the molecular structure of fatty acids is similar to the molecular structure in crude oil. Paraffin or methane series are straight-chain hydrocarbons having the general formula C_nH_{2n+2} while the naphthene series has carbon ring compounds having the general formula C_nH_{2n}. Thus, this hypothesis can be supported by the modern-day bio crude produced in the laboratory by hydrothermal and hydroprocessing technology, of algae and triglycerides. Although this is the most accepted theory for petroleum formation, an unanswered question is still there, how there were variations in the composition of crude oil, irrespective of their same biological origin.

The inorganic theory of petroleum formation initially proposed by Dmitri Mendeleev (1877), stated that metallic carbide reacted with water at high temperatures and produced acetylene which in turn converted to petroleum through condensation reaction as shown below:

$$\begin{tikzcd}
MC_2 + H_2O \arrow[r] & C_2H_2 + MO \arrow[d, "\text{Condensation}"] \\
 & C_nH_{2n+2} + C_nH_{2n}
\end{tikzcd}$$

This reaction is readily reproduced in the laboratory. Other inorganic theory was only the modification of the Mendeleev theory. Sometime later (during 1960) it was postulated that petroleum and gas reserves were produced the same way in the astronomical phenomenon that Jupiter, Saturn etc. had the methane in their formation. However, this hypothesis has the drawback of not having any proof of actual processes occurring deep inside the earth.

Whatever may be the process of formation and accumulation of crude oil, the quality and composition of the crude oil differs from reservoir to reservoir.

1.3.2 Classification of Crude Oil:

Crude oils are classified based on a specific standard of **the American Petroleum Institute** (API) called ° API.

$$^{o}\,API = (141.5/\,\text{Specific gravity}) - 131.5 \quad \text{...} \tag{1}$$

Specific gravity (SG) is measured as the ratio of the density of crude oil to the density of a reference substance, usually water at 60 ^{0}F. For measuring SG of crude oil normally manual hydrometer or automatic density meters are used. Crude oil is classified as **light, medium, or heavy** according to its measured API gravity. Light crude oil has an API gravity higher than 31.1° (i.e., less than 870 kg/m^3); Medium oil has an API gravity between 22.3 and 31.1° (i.e., 870 to 920 kg/m^3); Heavy crude oil has an API gravity below 22.3° (i.e., 920 to 1000 kg/m^3); Extra heavy oil has an API gravity below 10.0° (i.e., greater than 1000 kg/m^3).

For example, if a crude oil of Indian origin has an SG= 0.8765, the ° API calculated from formula (1) is equal to 30.02 and can be classified as a medium oil. Different classes of crude oil are found in different geographic locations and hence they are sometimes called region-specific, viz. Indian crude, North America's West Texas Intermediate crude (WTI), North Sea Brent Crude, and the UAE Dubai Crude etc.

Sometimes, crude oils are also classified as paraffinic, naphthenic, aromatic and asphaltic, based on their chemical composition. Individual components derived from the fractional and vacuum distillation of crude oils are further classified based on their **volatility (boiling range) and specific fuel properties.** Details will be discussed in the succeeding chapters.

A cumulative distillation of the crude oil at atmospheric and vacuum conditions is carried out on a laboratory scale using distillation equipment called True Boiling Point (TBP) distillation apparatus, which depicts the actual percentage of recoverable liquid or semisolid most often used as fuels as shown in **Fig.1. 3.** Higher the percentage recovery from the distillation better is the crude oil from refining and economic perspectives. The untitled residue is called the Bitumen, which has also multiple utility and good commercial value.

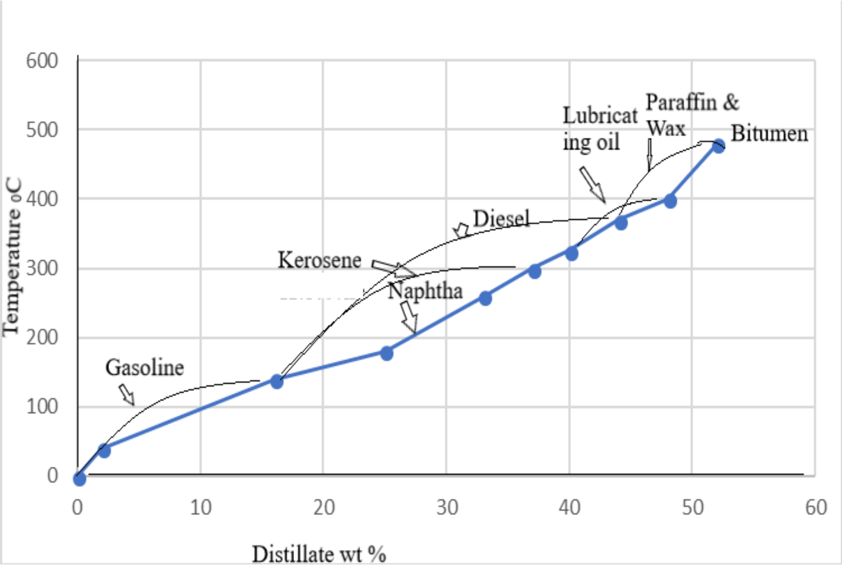

Fig. 1. 3. True boiling point distillation curve of petroleum crude oil.

A few research works were carried out for crude oil distillation, biocrude oil development and distillation: blending or without blending with crude oil (Sarma and Konwer, 2005, Aslam et al., 2015), use of the catalyst for further distillation of bitumen obtained from crude oil distillation using Simulated distillation (Sim Dis) process (Hashemi et al, 2013) etc. can be found in literature in the recent trend. Ryder and co-workers (2001-) made significant efforts to classify petroleum crude oil based on its fluorescence behaviour collected from different regions of the world. From their research, it was established that light oils (high API gravity) tend to have relatively narrow, intense fluorescence emission bands with small Stokes shifts, and longer fluorescence lifetimes when compared to heavy oils (low API gravity) where the emission tends to be weaker, broader, and red-shifted. These changes in fluorescence emission are due to the higher concentration of fluorophores and quenchers present in heavier oils, which leads to a higher rate of energy transfer and fluorescence quenching, producing broader, weaker, red-shifted emission (Sarma and Ryder, 2006).

1.4 Natural Gases

Natural Gases are classified based on their occurrences in the gas reservoir as **Associated Natural gases**, found in association with the petroleum reservoir and **Non-Associated Natural gases** found alone in the reservoir irrespective of nearby petroleum reservoir. The location of natural gases is just near the vicinity of crude oil reserves proving their biological origin and supporting the organic theory of petroleum formation. Of course, their origin from inorganic reactions or catastrophic astronomy phenomena cannot also be denied at a stretch, as methane-made planets are also available in the solar system.

At normal temperature and pressure (NTP), as the name implies, natural gases exist in the gaseous state. They can be liquified under varied temperatures and pressure. Natural gases on compression at high pressure (200 bar) form “compressed natural gas” (CNG)with significant reduction in volumes which can then be used as a fuel in cars, vans, and light trucks. Natural gas can be liquefied, resulting in “liquefied natural gas” (LNG) on cooling to -161°C and takes up just 1/600th the volume of the gaseous state. In this LNG form, it can be used as a fuel for ships and trucks and can be easily transported by ship over long distances. Based upon the percentage of methane content and calorific value (the most important property of any fuel, to be discussed in Chapter 2), natural gases can be further classified as high calorific value gas and low calorific value gas.

The composition of natural gases is tabulated in **Table 1.3** which varies for different reservoirs as per their geographic locations. As has been seen from Table 1.3 Russia has the best quality natural gas as high as

97.8%(vol) methane content, whereas India has also excellent quality natural gas reserves, although limited, in the Assam oilfield.

Table 1.3 Composition of Natural Gas Germany, USA, Russia, Iraq and India (Source: Narayanan and Viswanathan, 1997)

Gaseous composition (% Vol)	**Germany (Sub-Oldenburg)**	**USA (Texas)**	**Russia (Siberia)**	**Iraq (Kirkouk)**	**India (Assam)**
CO_2	6.9	….	….	2.7	0.4
N_2	7.0	25.6	1.2	….	1.7
H_2S	7.1	…..	…..	….	….
CH_4	78.9	65.8	97.8	59.6	93.2
C_2H_6	0.1	3.8	0.7	19.8	5.4
C_3H_8	….	1.7	0.3	5.5	2.1
C_4H_{10}	….	0.8	….	1.9	1.1
C_5 +	….	0.9	….	1.1	0.4
He	….	1.8	….	….	….

1.5 Biomass

Biomass is a renewable organic material that originates from plants and animals and is the primary fuel for cooking and heating even today in the rural areas of developing countries like Africa, Indonesia, India, Brazil etc., even though the Govt has been taking steps to connect every part with LPG. Many developed countries are using biomass fuels for transportation and electricity generation to avoid carbon dioxide emissions caused by fossil fuels. Biomass and waste account for 27% energy supply in the Indian scenario as per the International Energy Agency Report (IEA Report 2009). The biomass and dung are used for cooking in traditional and scientific cookstoves as such after drying or by producing Charcoal by the traditional pyrolysis method, as per the availability of the biomass and wastes in a particular region. In 2021, biomass provided about 4,835 trillion British thermal units (TBtu), or about 4.8 quadrillion Btu and equal to about 5% of total U.S. primary energy consumption. Of that amount, about 2,316 TBtu were from biofuels (mainly ethanol), 2,087 TBtu were from wood and wood-derived biomass, and 431 TBtu were from the biomass in municipal solid wastes and sewage, animal manure, and agricultural byproducts. The industrial and transportation sectors account for the largest amounts, in terms of energy content, and the largest percentage shares of total annual biomass consumption. The wood products and paper industries use biomass in combined heat and power plants to process heat and generate electricity for their use. Liquid biofuels account for most of the transportation sector's biomass consumption. The residential and commercial sectors use firewood and wood pellets for heating. The commercial sector also consumes, and in some cases, sells renewable natural gas produced at municipal sewage treatment facilities and waste landfills.

Biomass can be classified based on their growth pattern as fast growing and slow growing; composition and value addition: wood and wood processing wastes (firewood, wood pellets, and wood chips), crops and waste materials (corn, soybeans, sugar cane, switchgrass), Biogenic materials in municipal solid waste (paper, cotton, and wool products, and food, yard) and Animal manure and human sewage for producing biogas/renewable natural gas. The presence of cellulose, hemicellulose and lignin in different proportions in the composition makes every species unique concerning attribute for different applications. Furthermore, biomass can be converted to energy through various processes including direct combustion (burning) to produce heat, thermochemical conversion to produce solid, gaseous, and liquid fuels, chemical conversion to produce liquid fuels and biological conversion to produce liquid and gaseous fuels. The classification of the biomass based on their composition can be described as presented in **Fig. 1.4.**

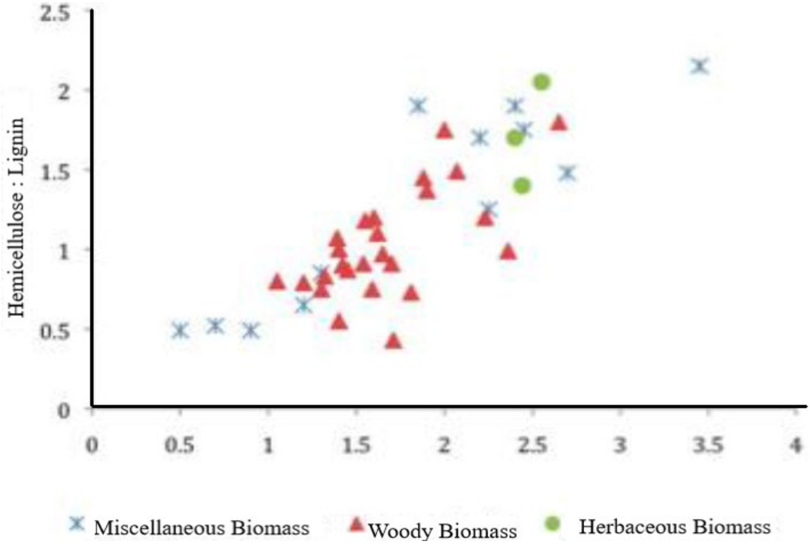

Fig. 1.4 Hemicellulose and cellulose variations with lignin for different biomass (Langille, 2009).

Biofuels are classified based on their generation type as their origin is from biomass. **First-generation biofuels (1G)** produced as a byproduct of the food chain such as sugar, starch, vegetable oil, or animal fats using conventional techniques e.g., biodiesel (from edible oil), Bio-alcohols, Vegetable oil, Bio-ethers, Biogas; **Second generation biofuels (2G)** are produced from non-food crops, such as cellulosic biofuels and waste biomass eg., advanced biofuels like biohydrogen, bio-methanol, biodiesel (nonedible oil), bioethanol (from lignocellulosic materials), green diesel, butanol (from biomass) etc.; **Third and fourth generation biofuels** (3G &4G) are derived from the secondary products of 1G and 2G biofuels using biological processes and from algal biomass. Details of biomass and biofuels will be discussed in the respective chapter.

Synthesis gas and producer gases are the products of biomass gasification, under very limited oxygen presence. The resulting gas mixture that contains CO and H_2 as the predominant constituents and the reaction efficacy can be described using a quaternary diagram as shown in **Fig. 1.5.**

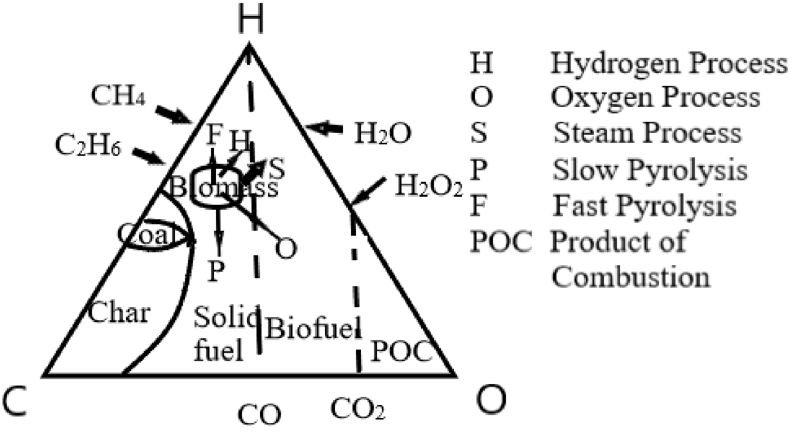

Fig. 1.5 Ternary diagram of carbon, hydrogen and oxygen compounds during biomass conversion process

The apex of the ternary diagram represents the elements C, O and H, the sides connecting two elements represent compounds formed by these two elements while the products in the face represent the presence of all three elements with varying compositions concerning their placement in the quaternary diagram. The sides opposite to the element represent its concentration as zero. Complete gasification and combustion processes can be described by using this ternary diagram. Different fuels can be categorically placed inside this ternary diagram with varying C, H and O stoichiometric composition.

1.6 Nuclear fuels

Nuclear fuels are classified as Nuclear fissile materials (Uranium, Thorium etc.) and nuclear fusion material (deuterium or heavy hydrogen etc.). The nuclear fuel chain liberates a huge amount of energy and the reaction is initiated with slow speed neutron and continues with the *in-situ* neutron liberated during the chain reactions. Although U^{238} is a radioactive nucleus, the nuclei with neutron-proton ratio between 1.17 – 1.52 are relatively stable and decayed upon excitation by fission nuclei either by beta emission or neutron emission. The control of the neutron speed is accomplished with boron or cadmium rod to control the overall chain reaction that occurs under 30 different pathways.

Nuclear Fission reaction

$$ {}_{92}U^{235} + {}_{0}n^{1} \longrightarrow {}_{36}Kr^{89} + {}_{56}Ba^{144} + 3\,{}_{0}n^{1} + 200\ \text{MeV} $$

$$ {}_{90}Th^{232} + {}_{0}n^{1}{}_{90} \longrightarrow Th^{233} + {}_{-1}e^{0} \rightarrow {}_{91}Pa^{233} + {}_{-1}e^{0} \rightarrow {}_{92}U^{233} $$

This implies fission reactions are exothermic and U^{235} and U^{233} are very much favorable for nuclear fission to produce heat and can be effectively utilized for power generation.

Nuclear Fusion reaction

Two lighter nuclei when bombarded and attained the coulomb barrier fuse to form a heavy nucleus releasing a substantial amount of energy. In general, the following four fusion reactions are possible:

$$ {}_{1}D^{2} + {}_{1}D^{2}{}_{2} \longrightarrow He^{3} + {}_{0}n^{1} + 3.27\ \text{MeV} $$

$$ {}_{1}D^{2} + {}_{1}D^{2}{}_{1}T^{3} + \longrightarrow {}_{1}H^{1} + 4.03\ \text{MeV} $$

$$ {}_{1}D^{2} + {}_{1}T^{3} \longrightarrow {}_{2}He^{4} + {}_{0}n^{1} + 17.6\ \text{MeV} $$

$$ {}_{1}D^{2} + {}_{2}He^{3} \longrightarrow {}_{2}He^{4} + {}_{1}n^{1} + 18.3\ \text{MeV} $$

The total energy released from the six deuterium nuclei is 43.2 MeV, and to cross the initial energy barrier sufficient energy is required to be provided. The details will be discussed in the chapter concerned with nuclear Energy.

1.7 New generation fuels, hydrogen, fuel cells

New generation fuels, hydrogen, fuel cells etc. have their classification based on the system of energy generation and the types of fuel and/or medium used will be illustrated in the individual chapters. The use of hydrogen and fuel cells is currently being found in space applications, and transportation in advanced machineries where the fuel is directly converted to electricity. LiH, pure hydrogen and boron hydrides are found in the literature for their use in engines as fuel and battery/ fuel cell applications. The details of the principle and working of fuel cells will be discussed in the succeeding chapters.

1.8 Green hydrogen as a fuel

Hydrogen is the most abundant chemical element on the planet and is present in 75 % of matter. It is, however, not found alone but in combination with other chemical elements such as oxygen and carbon that form water and organic compounds. Nonetheless, green hydrogen refers to hydrogen generated from renewable energy or from low-carbon power sources that do not emit pollutants. The carbon emissions from green hydrogen are significantly lower than those from grey hydrogen, which is produced by steam-reforming natural gas. The amount of green hydrogen produced from the electrolysis of water is less than 0.1% of the total amount of hydrogen produced. As a result, it can help limit climate change by decarbonizing sectors that are difficult to electrify, such as steel and cement production. In addition to blending green hydrogen into natural gas pipelines, it can also be used to make green ammonia, which is the main component of fertilizers.

1.8.1 Generation of green hydrogen

Production of green hydrogen is done by the electrolysis from renewable sources which includes the breaking of water molecules (H_2O) into oxygen (O_2) and hydrogen (H_2). During electrolysis, the water used must contain salts and minerals to conduct electricity. A direct current is applied to two electrodes immersed in the water and connected to a power source.

Hydrogen and oxygen dissociate when electrodes attract ions with opposite charges. Electricity causes an oxidation-reduction reaction during electrolysis. The produced oxygen from electrolysis can be directly sent to industries and hospitals for further usage.

In addition, the availability of several renewable sources also helps in the generation of hydrogen more effectively and maintains sustainability. These sources include rice straw, bagasse, corn stalk, potato waste, apple pomace, corn stover, and other municipal and agricultural wastes. All these wastes are generated in a surplus amount in different regions of the world. These sources can be effectively converted or transformed to produce green hydrogen via several processes including Natural Gas Reforming/Gasification, Electrolysis, Renewable Liquid Reforming, Fermentation, and Fermentation. While several hydrogen production methods are still in development including High-Temperature Water Splitting, Photobiological Water Splitting and Photoelectrochemical Water Splitting, and I-S-cycle hydrogen production technology.

Natural Gas Reforming/Gasification: Synthesis gas (a mixture of hydrogen, carbon monoxide, and a small amount of carbon dioxide) is produced by reacting natural gas with high-temperature steam. Hydrogen is produced by reacting carbon monoxide with water. Compared to other methods, this is the most effective, cheapest, and most common. Approximately 80% of hydrogen produced in the United States is produced by steam reforming of natural gas.

The synthesis gas can also be created in a pressurized gasifier by reacting coal or biomass with high-temperature steam and oxygen. Gasification is the process of converting coal or biomass into gaseous components. The resulting synthesis gas contains hydrogen and carbon monoxide, which react with steam to produce the hydrogen.

Renewable Liquid Reforming: Renewable liquid fuels, such as ethanol, methanol is reacted with high-temperature steam to produce hydrogen.

Fermentation: The conversion of biomass into sugar-rich feedstocks can result in hydrogen production via fermentation.

High-Temperature Water Splitting: High temperatures generated by solar concentrators or nuclear reactors drive chemical reactions that split water to produce hydrogen.

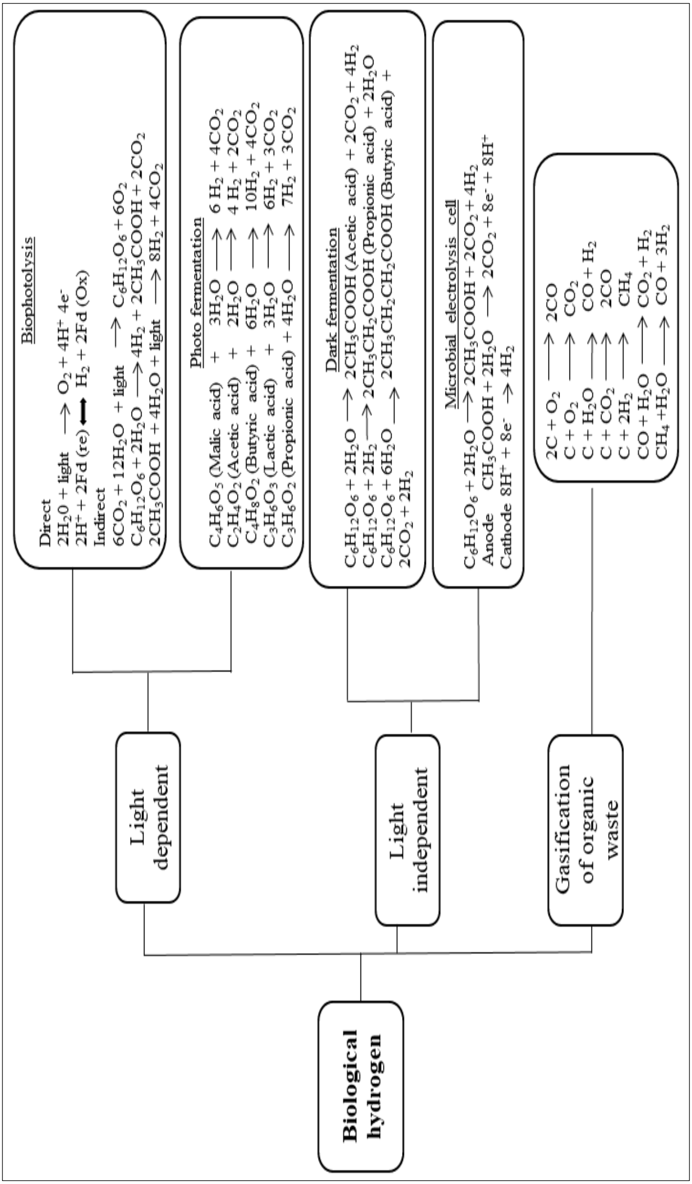

Fig. 1.6 Production of biohydrogen via biological processes (Rao R and Basak N 2021)

Photobiological Water Splitting: Microbes, such as green algae, consume water in the presence of sunlight and produce hydrogen as a byproduct.

Photoelectrochemical Water Splitting: Photoelectrochemical systems produce hydrogen from water using special semiconductors and energy from sunlight.

Advantages of green hydrogen

- **100 % sustainable**: During combustion or production, green hydrogen emits no pollution.
- **Storable**: Hydrogen is easy to store, which allows it to be used subsequently for other purposes and at times other than immediately after its production.
- **Versatile**: Hydrogen can be converted into electricity or synthetic gas and used commercially, industrially, or for transportation.

Disadvantages of green hydrogen

- **High cost**: Energy derived from renewable sources is the key to generating green hydrogen through electrolysis, which is more expensive to generate, which in turn makes hydrogen more expensive to obtain.
- **High energy consumption**: Hydrogen production in general and green hydrogen production in particular require more energy than other fuels.
- **Safety issues**: Due to hydrogen's high volatility and flammability, extensive safety measures must be taken to prevent leaks and explosions.

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