CHAPTER 1

INTRODUCTION

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1.1. Energy overview

Due to rapid development of technology and industrialization the energy consumption is increasing day by day. Today, fossil fuels are being predominantly used to fulfil these skyrocketing global demands for energy. Fossil fuels are not only used primarily for heat and power production, but also production of chemicals and liquid fuels for the transportation sector. By this way fossil fuels play a very important role in the society. It was reported that in 2011 the annual change in primary global energy demand was 188 million tonnes of oil equivalent (Mtoe) which is further increased to 328 Mtoe in 2018 as shown in Figure 1.1 (IEA,2018).

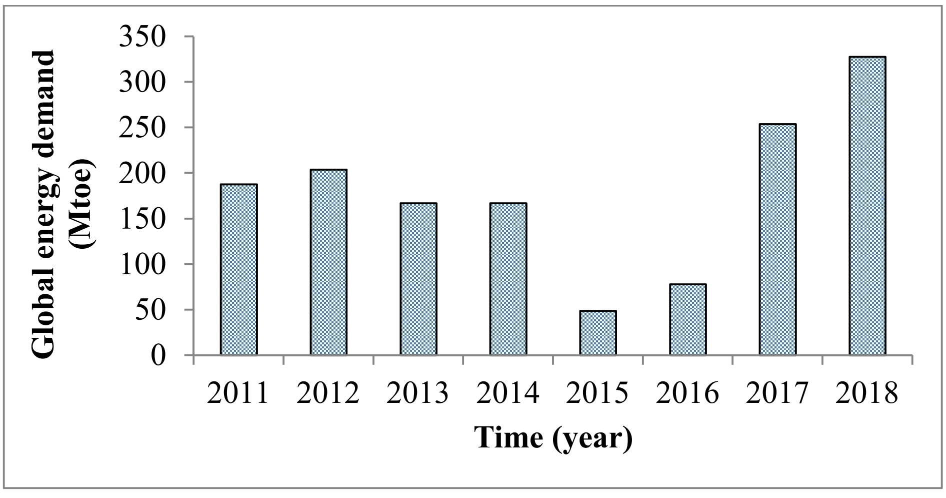

Figure 1.1 Changes in global primary energy demand during 2011-2018
(Source: IEA 2018)

The uses of fossil fuels have faced mankind with two major concerns: a) depletion of fossil energy resources and, b) deterioration of the environment by adverse environmental impacts due to release of significant number of pollutants such as NO_X, SO_X, particulates and CO_2. As shown in Figure 1.2, the release of CO_2 in atmosphere from fossil fuels was only 20.5 gigatonnes (Gt) in 1999 which increased gradually and reached to historic high 33.2 Gt in 2018 (IEA, 2018). Eventually it might have a direct reverberation in the rate of greenhouse gases and eventually promoting global warming.

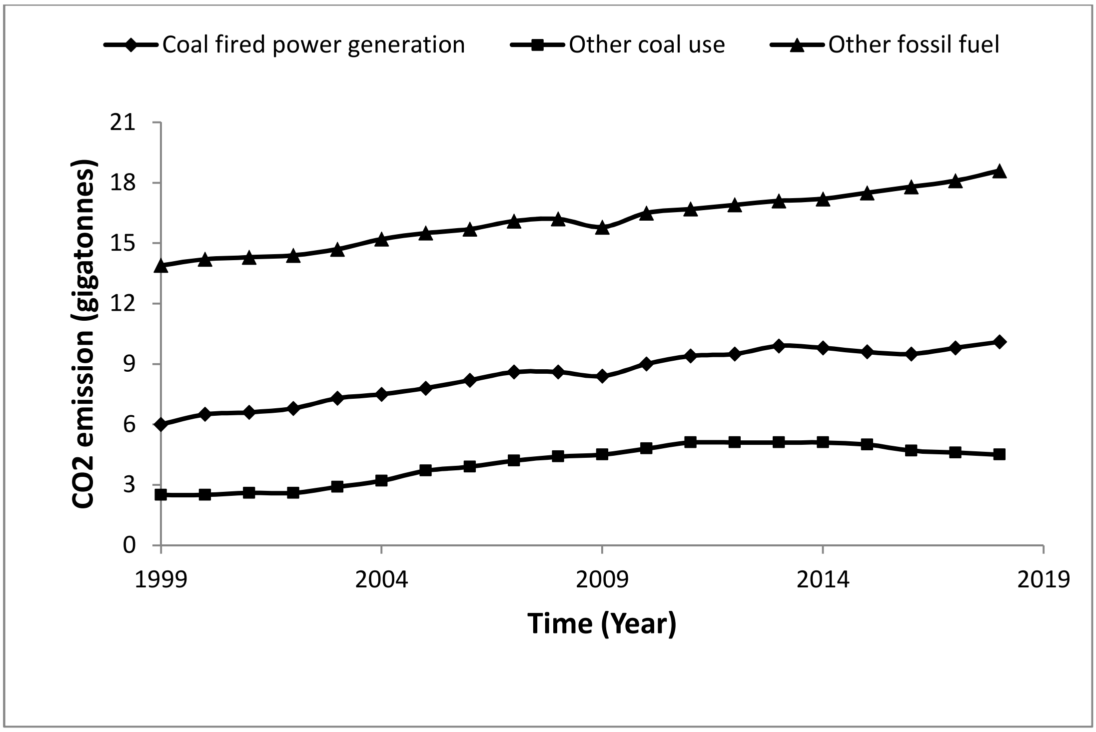

Figure 1.2 Global energy related CO_2 emissions by fossil energy source, 1999-2018 (Source: IEA, 2018)

Meanwhile, fossil fuels are not homogeneously distributed across the planet but concentrated in a few regions. It creates a big concern on the security of supply. Moreover, historically and recently, the power over fossil fuels is a root of many national and international conflicts since it is a business that moves a lot of money. Cheap and easy oilfields are the first to be operated consequently the first ones to be depleted. To meet a constant demand, more investments need to be done as easy oil fields become exhausted. Therefore, its price is also catapulting day by day and it is likely to follow more escalating tendency in the next decades because of irreversible consumption. However, as per current rate of consumption world's oil reservoirs will be diminished by 2050 (Alaudin et al., 2010) which were accumulated over aeons of geological activity. This will increase speculators and it will create a distortion on the demand of oil and ultimately on the price. This draws attention of researchers to find alternative of fossil fuels and it assuages to harness the energy and chemicals by assessing renewable sources.

1.2. Renewable energy

Renewable energy is the energy obtained from renewable resources, which are naturally replenished on a human timescale, such as solar, wind, tidal, waves, geothermal, energy from biomass, etc. Renewable energy often provides energy via electricity generation, air and water heating/cooling, transportation and rural (off-grid) energy services.

In 2009 over 80% of the energy consumption was generated from fossil fuels (Escobar et al., 2009) whereas, in 2018 the use of renewable energy increased and fossil fuels counted for about 75% (IEA, 2018) as shown in Figure 1.3.

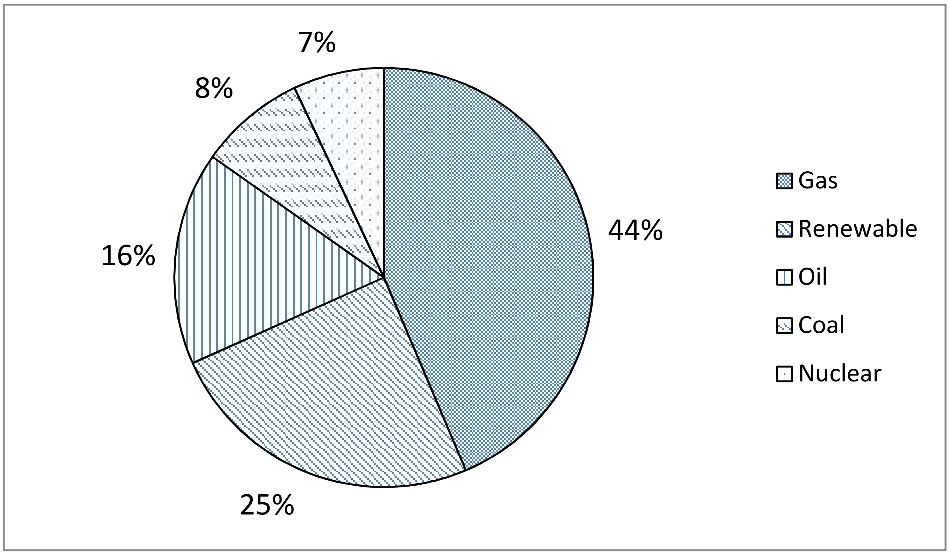

Figure 1.3 Energy demand met by individual energy resources in 2018 (Source: IEA, 2018)

In total renewable energy growth, China has highest contribution followed by Europe. The China and Europe were individually contributed more than rest of the world excluding United States and India (shown in Figure 1.4).

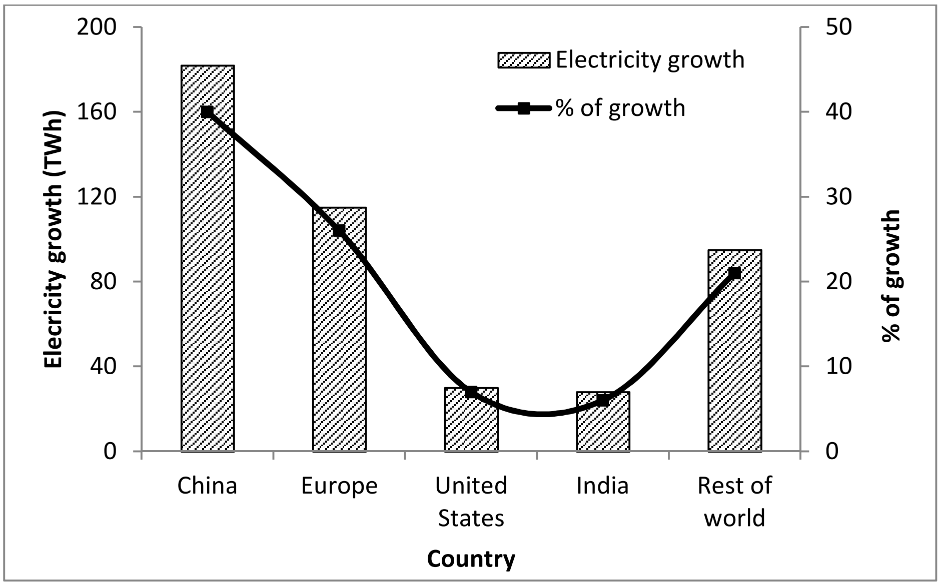

Figure 1.4 Growth in electricity generation by renewable energy sources as individual country, 2017-18 (Source: IEA, 2018)

However, as shown in Figure 1.5, solar photo voltaic, hydropower, and wind each accounted for about one-third of the growth with bioenergy accounting for the majority of the rest. Taken together, renewables were responsible for almost 45% of the world's increase in electricity generation. They now account for almost 25% of global power output as second after coal. Though, use of solar photo voltaic, hydropower and wind are already going on, however, it is limited to certain time and location. Furthermore, these sources of energies are limited to power generation and, still it will need to depend on fossil fuels for chemicals. Thus, researchers and scientists are still investigating for other globally available renewable sources of energy and chemicals.

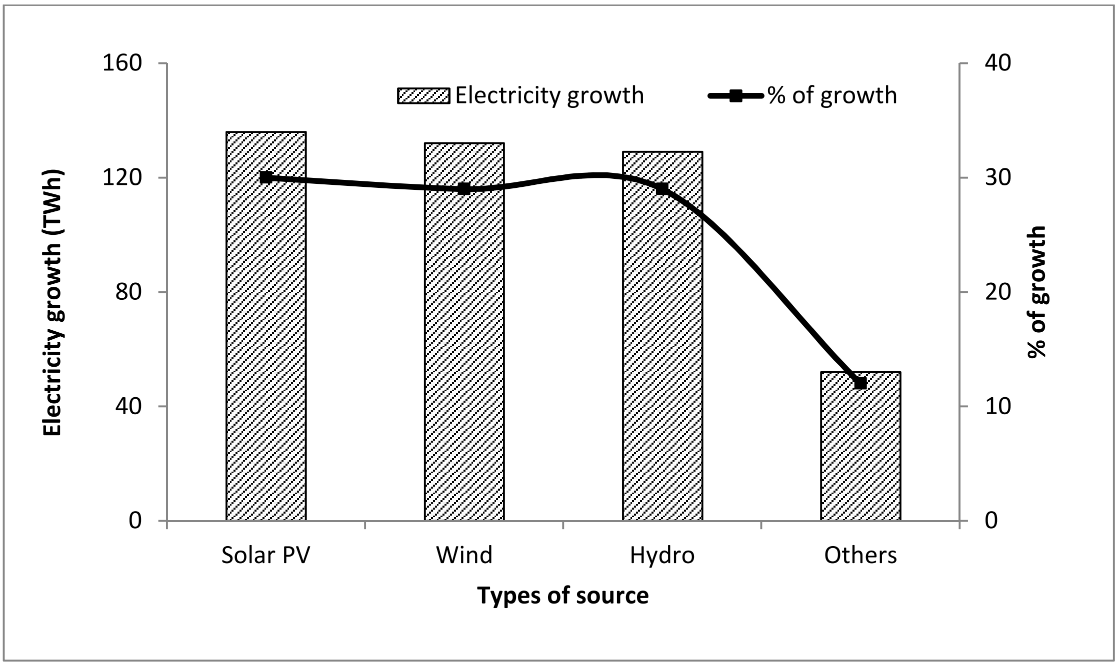

Figure 1.5 Growth in electricity generation by renewable energy sources 2017-18 (Source: IEA, 2018)

1.3. Biomass

1.3.1. Sources and types of biomass

Biomass is formed from living and living species like plants and animals (Basu, 2010). It mainly consists of carbon, hydrogen, oxygen and nitrogen which includes various natural and naturally derived materials such as woody and herbaceous species, wood wastes, bagasse, agricultural and industrial residues, waste paper, municipal solid waste, sawdust, bio solids, grass, food processing waste, animal wastes, aquatic plants, algae, etc. (Yaman, 2004). Moreover, it is most often referred to plants or plant-based materials which are not used for food or feed and are specifically known as lignocellulosic biomass. Some of the categorization of biomass has been listed in Table 1.1.

Table 1.1 Categorization of biomass and sources (Islas et al., 2019)

Sl. no.	Types of biomass	Sources
1	Woody biomass	Branches, chips, pellets, whole wood of trees, etc.
2	Herbaceous biomass	Residual part of cereal crops, pastures, oilseed crops, tubers and legumes, flowers, etc.
3	Municipal waste	food waste, paper, cardboard, plastics, textiles, wood, parks, etc.
4	Agro-industrial wastes	waste from the fruit canning industry, fruit mixtures, bagasse and husks, etc.

Since, all living creatures need food to sustain their life. In order to fulfil the requirement of food farmers need to grow crops, which generates huge amount of wastes. These wastes generate negative economic value to the farmers.

1.3.2. Generation and disposal of biomass

The biomasses generated from agricultural wastes are easily available everywhere on the earth. Furthermore, increasing population of world is in demand of huge amount of food. Thus, agricultural wastes are increasing day by day which is inevitable and cannot be abolished. Coconut is grown in more than 86 countries (BGCI, 2019) worldwide, with a total production of about 67128 million nuts in 2016 (CDB, MAFW, 2019). India occupies the premier position in the world with an annual production of about 13 billion nuts, whereas, two other prominent coconut producing countries are Indonesia and the Philippines.

Table 1.2 All India final estimates of area and production of coconut 2016-17(HD, MAFW, 2019)

Sl No.	States /Union Territories	Area (''000 Hectares)	Production (Million nuts)	Productivity (Nuts/ha)
1	Andhra Pradesh	115.21	1,377.53	11,957
2	Assam	20.60	153.27	7,440
3	Bihar	14.90	141.09	9,469
4	Chhattisgarh	1.48	8.77	5,926
5	Gujarat	24.44	336.65	13,775
6	Karnataka	513.85	6,773.05	13,181
7	Kerala	770.79	7,448.65	9,664
8	Maharashtra	20.90	198.85	9,514
9	Nagaland	0.47	2.67	5,681
10	Odisha	50.91	341.68	6,711

11	West Bengal	29.63	374.56	12,641
12	Tamil Nadu	461.06	6,570.63	14,251
13	Telengana	0.50	2.09	4,180
14	Tripura	4.61	32.23	6,991
15	Others	52.76	142.38	2,699
	Total	**2,082.11**	**23,904.10**	**11,481**

Moreover, Kerla is main coconut producing state followed by Tamilnadu, Karnatka and Andhra Pradesh. These four southern states together contribute to about 90 % of the total production in the country as shown in Table 1.2. Furthermore, the green coconut crop is also produced in several countries including Brazil because of the growing global demand for coconut products such as coconut water, coconut oil, coconut milk and coconut meat (Rodrigues et al., 2018; Gonçalves et al., 2015). However, a green coconut (unripe coconut) generates about 80 % of total mass as waste.

Some of the agricultural wastes like wheat straw, rice straw, etc. are completely utilized as cattle fodder. Besides these, sugarcane, sesame seed straw and mustered oil straw are burnt in the field whereas banana and papaya straws are left in the field for natural rotting and degradation but the green coconut coir do not degrade easily thus, it becomes disposal problems for farmers. Moreover, it gives suitable place for microorganism to grow on its surface. Thus, proper disposal of these wastes are very important for the good hygiene of the society.

1.3.3. Biomass: a potential source of energy

One of the globally available and most wasted renewable sources of energy is wide varieties of lignocellulosic biomass. It has been main energy source from the time of discovery of fire and it is still being used for heating and cooking purposes in rural areas.

During photosynthesis the solar energy with the combination of CO_2 and water is stored in the form of chemical energy as bonds of the structural components of biomass. If biomass is processed efficiently, either thermo chemically or biologically, the energy stored in the chemical bonds can be extracted with the release of energy, water vapour and CO_2. The process is cyclic, as the CO_2 is then available to produce new biomass. Biomass can be used for production of heat and power, and also for production of chemicals, liquid fuels for the transportation sector. Because biomass absorbs CO_2 from the atmosphere during growth and the combustion of biomass is associated with neutral CO_2 emission. As biomass is a renewable resource that is available almost all over the earth, thus, the security of supply is also much higher than for fossil fuels. For the production of heat and power, some other alternatives to fossil fuels such as solar PV, hydropower, wind and nuclear energy are exist, but for production of hydrocarbon chemicals, these alternatives cannot be used, besides biomass. Nevertheless, the low energy density of the biomass requires development and improvement in conversion technologies in order to increase process efficiency and reduce pollution.

1.4. Biomass to energy conversion pathways

Chemical energy stored in biomass can be converted into different forms of energy by using various processes. A general overview of biomass conversion pathways has been given in Figure 1.7. Many factors affecting the choice of the process include quantity of biomass feedstock, desired energy form, environmental standards, economic conditions and project specific factors.

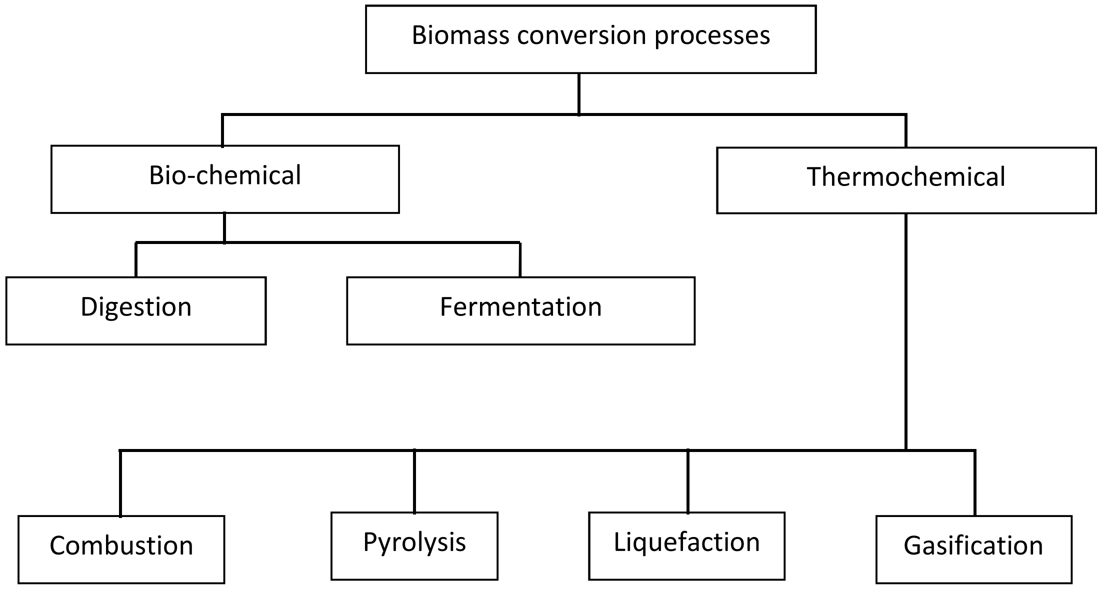

Figure 1.7 Overview of biomass conversion pathways

1.4.1. Biochemical conversion pathways

Biochemical conversion makes use of the enzymes or bacteria and/or other living organisms to break down biomass and convert it into fuels. This conversion process includes anaerobic digestion process and fermentation.

Anaerobic digestion process is a process in which organic material directly converted to a mixture of gases by some selective microorganism in the absence of O_2. The produced gaseous mixture contains primarily CH_4, CO_2 and H_2S in small a quantity which is collectively known as biogas. This process is suitable for organic waste having high moisture content about 70-90 %. The steps of this conversion process are hydrolysis, acidogenesis, acetogenesis and methanogenesis as shown in Figure 1.8. Solid residue that comes from digester is used as bio-fertilizer.

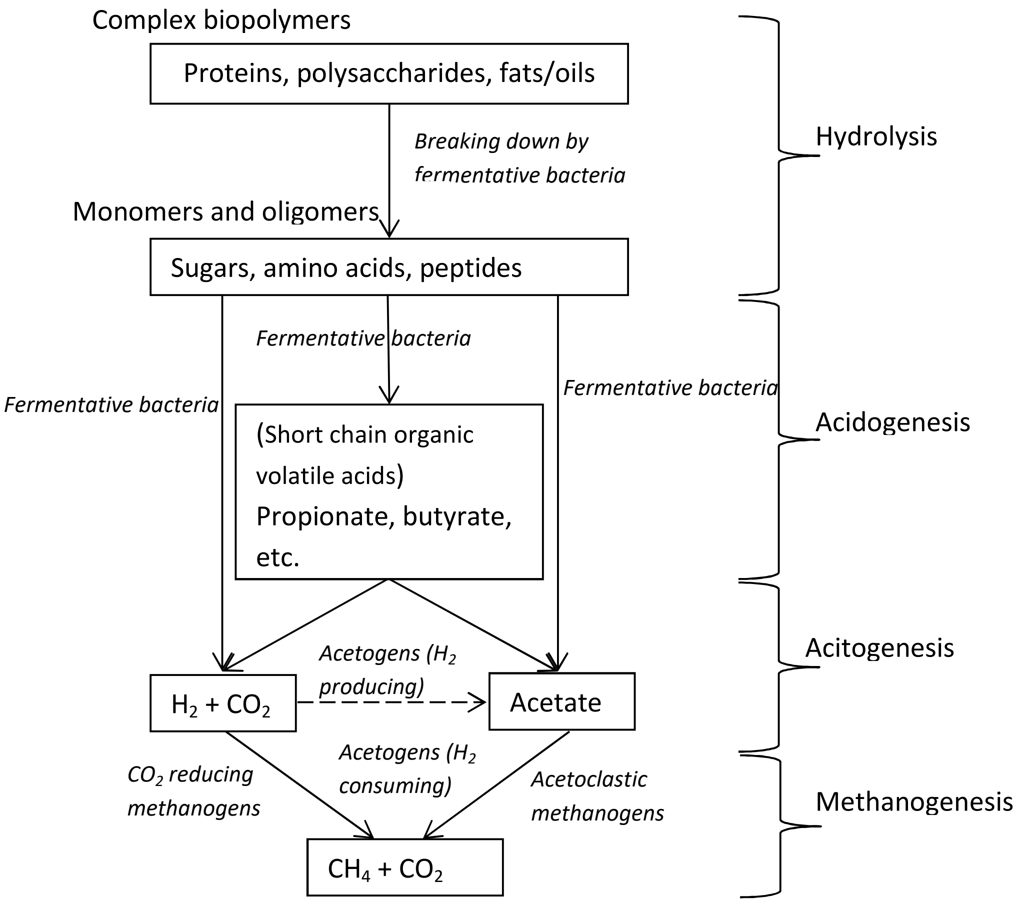

Figure 1.8 Anaerobic digestion process indicating four phases of conversion process

Fermentation is an anaerobic process that breaks down the glucose within organic materials with the yeast or bacteria and shown in Figure 1.9. The new generation fermentation process implies the conversion of a plant's glucose or carbohydrate into an alcohol or acid. Yeast or bacteria uses plant's derived sugars as a food and excrete ethanol/butanol and carbon dioxide. These can be further distilled and dehydrated to achieve higher concentration of alcohol which can be useful for automotive fuel. The solid residue from the fermentation process is used as cattle-feed or in some cases it is used as fuel for boilers or for subsequent gasification.

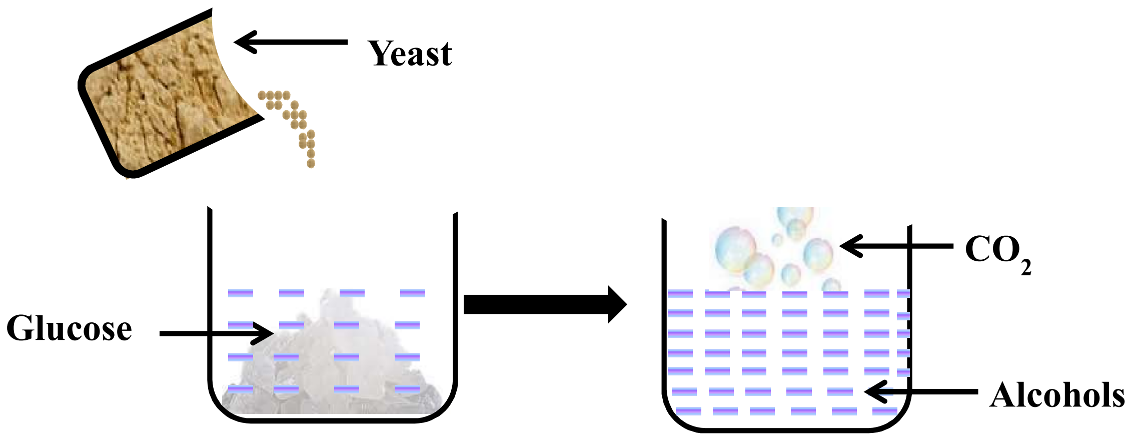

Figure 1.9 Fermentation process

1.4.2. Thermochemical conversion pathways

In thermochemical conversion pathways, bonds between adjacent carbon, hydrogen and oxygen molecules are broken down to release their stored chemical energy that were stored during the process of photosynthesis. Thermochemical conversion includes combustion, pyrolysis, liquefaction and gasification. A general overview of the thermochemical process is shown in Figure 1.10.

During all the thermochemical conversion of biomass, the process changes with the amount of O_2. The thermochemical conversion with excess amount of O_2 is known as combustion whereas, the conversion O_2 without supply is known as pyrolysis. Furthermore, limited amount of supply of O_2 during thermochemical conversion is known as gasification. All processes have significant characteristics as listed in Table 1.3.

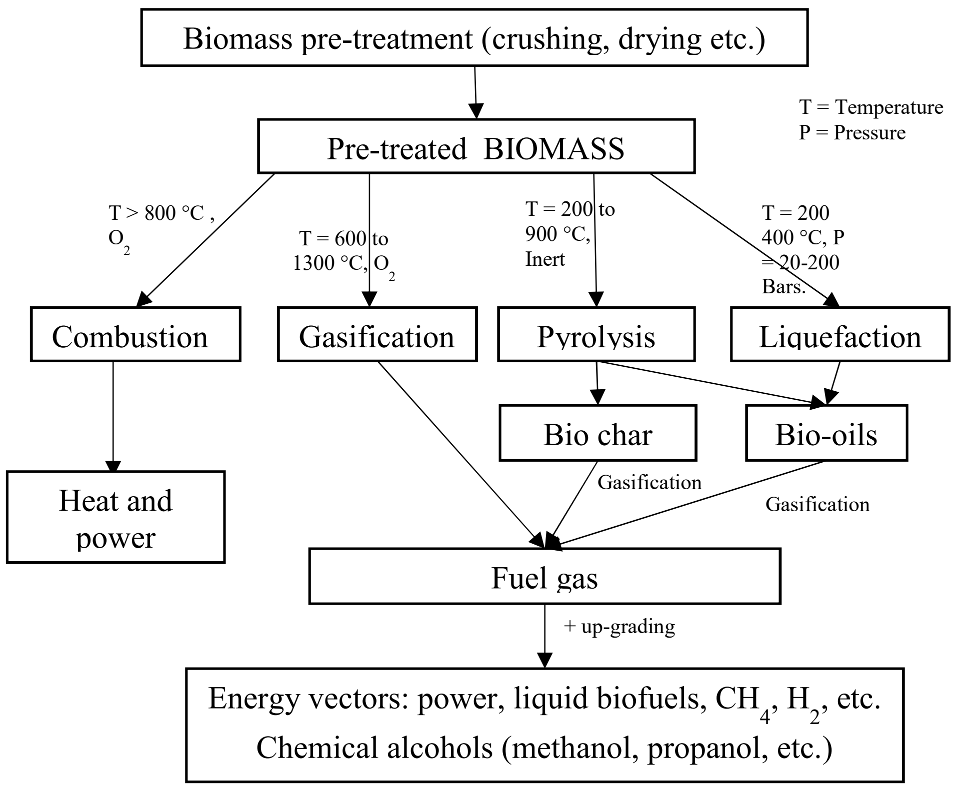

Figure 1.10 Overview of main thermochemical process

Table 1.3 Characteristics of thermochemical process

Sl. No.	Process	Amount of oxygen	Process temperature (°C)	Useful products
1	Combustion	Excess	above 800	Heat
2	Gasification	Limited	700-1100	gas
3	Pyrolysis	Absence	350-550	Char, bio-oil
4	Liquefaction	Limited	250-400 (High pressure; 4-22 Mpa)	Bio-oil

1.5. Gasification

1.5.1. General process of biomass gasification

In all available thermochemical processes, gasification is an energy efficient thermochemical process that converts carbonaceous materials like biomass into useful convenient gaseous fuels or chemical feedstock through partial thermal oxidation of biomass. The produced gaseous mixture is mainly composed of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2) and methane (CH_4). The produced gaseous mixture is often called synthesis gas/producer gas or fuel gas that can be used for heat production, generation of electrical power or further can be processed into chemicals or transport fuels. Hydrogenation or hydrogasification involves adding hydrogen to carbon to produce fuel with a higher hydrogen-to-carbon (H/C) ratio is also gaining popularity.

Gasification processes are carried out in different types of gasifiers such as fixed bed, moving bed, fluidized bed, entrained flow gasifier, etc. However, widely used gasifiers are fixed and fluidized bed gasifier. Fixed bed gasifier (updraft & downdraft) which is simple in design and operation whereas, second is fluidized bed gasifier. Fluidized bed gasifiers have relatively good contact of solids with gasifying medium, excellent heat transfer characteristics and thus increase the efficiency as compared to fixed bed gasifier (Basu, 2006; Basu, 2010).

1.5.2. Biomass selection criteria

For the gasification, biomass should have (Sanchez-Silva et. al., 2012):

- High volatile matter
- High calorific value
- Low ash content
- Low moisture content

- locally available biomass
- Not easily degradable (easily degradable will go for anaerobic digestion and fermentation)

1.5.3. General chemistry of biomass gasification

As gasification is the conversion of biomass to a gaseous fuel by heating in a gasification medium such as air or steam with restricted amount of oxygen. The process involves the steps such as drying, pyrolysis, oxidation and reduction (Antonopoulos et. al., 2012).

Usually, biomass suitable for gasification process contains 10-30% moisture. When biomass is heated up to about 100 °C, the moisture is converted into water vapour. After drying, as heating continues, the biomass undergoes pyrolysis. Pyrolysis is heating the biomass between 300-550 °C without supplying any oxygen. As a result, the biomass is decomposed into solids, liquids, and gases. Charcoal is the solid, tar is the liquid, and fuel gas is the gaseous product. Air is introduced into the gasifier after the decomposition process. During oxidation charcoal or the solid carbonized fuel reacts with the oxygen in the air at about 700–1000 °C to produce carbon dioxide and heat. Furthermore, at higher temperatures under reducing condition the following reactions take place to produce carbon dioxide, hydrogen, and methane (Zhao et al., 2016; Cabuk et al., 2019).

$$Biomass \rightarrow H_2 + CO + CO_2 + CH_4 + HC(g) + Tar(l) + Char(s) \quad (1.1)$$

$$C + CO_2 \rightarrow 2CO \qquad \Delta H = +172 \text{ kJ/mol} \quad (1.2)$$

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H = +131 \text{kJ/mol} \quad (1.3)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41.98 \text{ kJ/mol} \quad (1.4)$$

$$CH_4 + H_2O(g) \rightarrow CO + 3H_2 \qquad \Delta H = +206 \text{ kJ/mol} \quad (1.5)$$

$$Tar + H_2O(g) \rightarrow CO + CH_4 + H_2 + C_nH_m \quad (1.6)$$

$$C_nH_m + nH_2O \rightarrow nCO + [n + \left(\frac{m}{2}\right) H_2] \quad (1.7)$$

Thus, as per equation 1.2 addition of CO_2 with gasification medium will increase the CO in fuel gas which occurs above 500 °C but a significant amount of CO_2 gets converted to CO above 800 °C. Likewise, steam reacts with CO, CO_2, and CH_4 producing H_2. Therefore, steam gasification increases the production of H_2 compared to air gasification.

1.6. Technical difficulties of gasification process

It can be seen clearly from equations (1.4) to (1.7) that water in vapour form has very important role in formation of H_2 content in the produced gas. To fulfil the purpose, steam is being provided as gasifying medium. Furthermore, to provide favourable condition to split H-O-H bond from water vapour, researchers and scientists started using catalyst (Maa et al., 2019; Wang et al., 2016; Zhang et al., 2015). Thus, many types of catalyst (synthesized and natural occurring) have been used so far. However, if the gasifiers are 'air blown', atmospheric nitrogen dilutes the fuel gas to a level of 10-14%.

1.7. Origin of the problem

The outer part of coconut shell is not easily degradable so it cannot be left in the agricultural field. Thus, farmers need to spend money for its disposal. Also, coconut husk contains a high amount of lignin composition, so it cannot be easily hydrolysed by enzymes. Hence, it cannot be used for energy production through biochemical route. However, thermochemical process like gasification could be a better option to utilize this waste for energy production. Furthermore, it would be better if it can utilize waste of an industry. Moreover, none of the research has been found on gasification utilizing paper and pulp waste water as a source of catalyst since it contains metals like Ni, Fe, Zn and Na, etc. (Thompson et al., 2001; Lacorte et al., 2003) which could be impregnated into the biomass to enhance the H_2 content in the fuel gas rather using conventional catalysts.

1.8. Objectives of the present work

Based on above problems, following objectives have been decided for the Ph.D. work:

- To prepare and characterize unripe coconut husk for the study of fixed and fluidized bed gasification
- To use humidified air as gasifying medium instead of steam
- To use paper and pulp industry waste water as source of metals for catalyst to be impregnated onto unripe coconut husk for higher gas yield and H_2 content in the fuel gas
- To study the effect of CO_2 addition with the gasifying medium on higher heating value of the fuel gas
- To optimize the fluidized bed process parameters for maximizing H_2, CO, and minimizing CH_4, CO_2 content in the fuel gas using response surface methodology (RSM)