Chapter 1

Introduction

1.1 Overview

This chapter presents the motivation behind the purpose of carrying out the present study on the pretreatment of biomass to enhance the bio-fuel properties. A brief introduction on biomass and its sources has been covered. This chapter also includes a brief discussion on biomass pretreatment and its pyrolysis. In the last part of this chapter, contributions and thesis structure have been provided.

1.2 Motivation

Generation of sustainable energy from alternate fuels has become the need of the hour due to rapid depletion of fossil fuels and environmental concerns associated with the usage of these. Biomass as one of the alternate sources for fuel generation provides around 10% of the world's annual energy demand (Chen et al., 2012) and has become very promising due to its zero carbon footprint, abundant availability and being relatively less expensive (Lee et al., 2012). A major portion of population present in the underdeveloped and developing nations lives in rural areas, and they depend heavily on agricultural goods for their survival which play a very important role on improving their socioeconomic standards. For developing countries like India, agriculture is the backbone of the economy. Agricultural products during each stage of development produces large amount of biomass which mostly remains underutilized and fetches a mere economic value. For example, India currently produces 611 million tons per year of agricultural residue (Cardoen et al., 2015), which can be utilized for setting up potential biomass-based industries and can help in improving the economic backwardness of developing, and underdeveloped nations.

Although potentially biomass has a great scope to meet the energy needs, still its application for the same has been limited due to some disadvantages associated with the use of raw biomass such as high moisture content, highly hygroscopic in nature, low energy density, low heating value and logistics issues (Gong et al., 2019; Wang et al., 2018). Pretreatment process like torrefaction can be used to overcome some of these drawbacks associated with the usage of raw biomass in processes such as combustion, gasification and pyrolysis.

Bio-oil, the liquid condensate obtained after the pyrolysis of raw biomass has high content of oxygenates and water due to which it needs further treatment or upgrading to be utilized as a drop-in fuel in internal combustion engines. However, it would be beneficial if the bio-oil obtained after pyrolysis could contain less water and oxygenated groups, one such possible way could be pyrolysis of torrefied biomass and can help in reducing the cost involved in upgrading of bio-oil. It is also worth mentioning that both torrefaction and pyrolysis involve external energy input for producing torrefied biomass and bio-oil, respectively. Hence, the current research focuses on the process optimization of both torrefaction and pyrolysis for the production of high grade bio-fuels along with their energy-exergy analysis to improve the existing processes by introducing energy recuperation from by-products, and thus decreasing the involved energy consumption.

1.3 Biomass and its Sources

Biomass can be defined as a material obtained from a living or recently living species, e.g., plants, animals etc. Biomass obtained from plants or trees is basically produced via photosynthesis wherein a plant absorbs carbon dioxide, moisture and sunlight to produce biomass and liberates oxygen. It basically consists of three main components that are hemicellulose, cellulose and lignin with small amount of extractives. Biomass generally contains 20-40 wt% (Bajpai, 2020; Dhyani and Bhaskar, 2019) of hemicellulose which is amorphous in nature and has a degree of polymerization on the lower side. Hemicellulose contributes to the most of the acetic acid produced during pyrolysis. Cellulose, on the other hand generally constitutes 35-55 wt% (Hu et al., 2020) of biomass and as a result of vander Waal's forces and hydrogen bonding, cellulose has microfibril crystalline structures with higher thermal resistance as compared to hemicellulose. Cellulose during pyrolysis contributes maximum to the bio-oil yield. Lignin forms rest of the biomass component and is a cross linked amorphous resin which acts as a binder for the cellulose microfibrils. Lignin consists of a highly branched heterogeneous polymer which readily depolymerizes and during pyrolysis, bio-char is mainly obtained from lignin.

When biomass is burnt to harvest energy or heat, it undergoes combustion, thereby, producing carbon dioxide which was actually absorbed by the plants from the atmosphere. Hence, biomass is also called "carbon dioxide neutral". It is known from compositional analysis of biomass that it has very little or no sulfur content. Besides, biomass does not need millions of years to grow; actually it takes from a couple of months to a couple of years for the completion of growth of biomass making it a renewable material. Due to these reasons, biomass becomes an attractive candidate for harnessing renewable energy. It may be noted that the portion of biomass which is used for human consumption as food, is normally not called biomass from energy viewpoint. As an example, entire rice plant is biomass as per definition; however only rice husk and rice straw are considered as biomass for harvesting renewable energy.

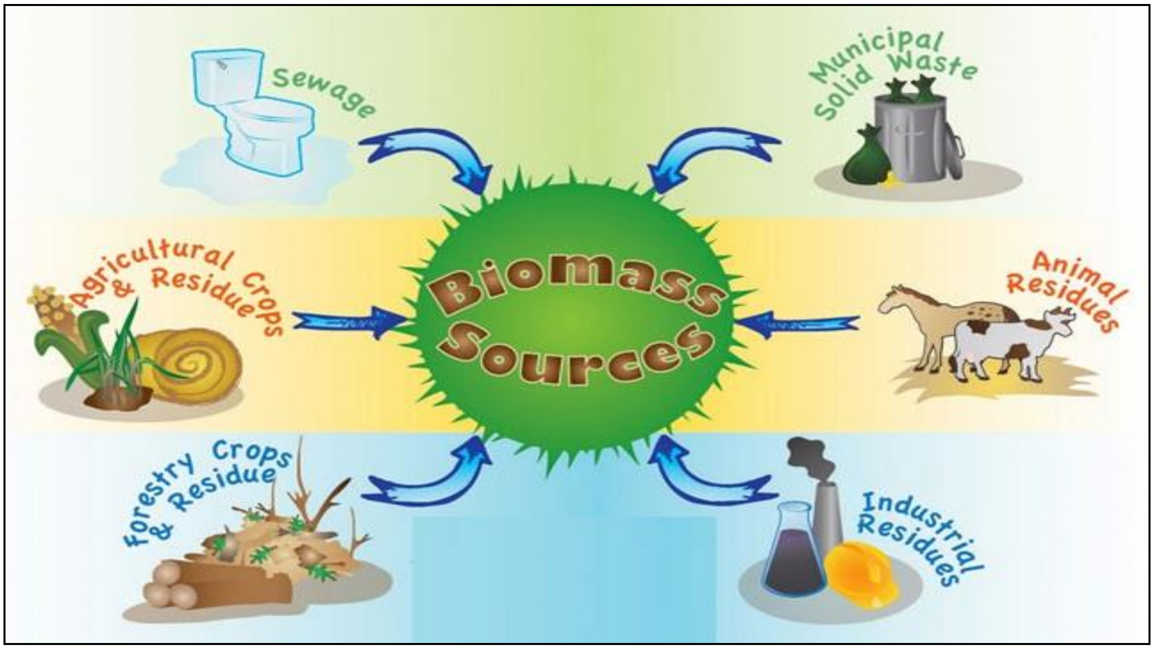

Fig. 1.1 Different sources of biomass (Bar-On et al., 2018).

Waste biomass is that portion of biomass which is not consumed by human being or animals. Generally the different sources of biomass can be observed from Fig.1.1 and in the present study the research is focused on two broad categories, i.e. agricultural and forest residue. Fortunately, many countries in Africa, South-Asia and Latin America have rich source of both types of waste biomass. Easy availability of biomass coupled with limited reserves of crude oil creates huge opportunity for scientists and engineers to fast-track research on renewable biomass and commercialization of developed technology.

1.4 Biomass Pretreatment

It is a well-established fact that even though the availability of biomass on the planet Earth is abundant, its use in energy or fuel generation has certain limitations due to various cost incurred at different stages of its processing. The use of raw biomass as a feedstock for generating fuel or energy has few drawbacks due to its poor physicochemical properties. Bio-oil obtained from pyrolysis of raw biomass has poor properties such as low HHV, high instability, high oxygen and water content, low hydrogen content and being acidic in nature due to which such bio-oils needs upgradation before being used as a transportation fuel or for producing different biochemicals. The cost of producing transportation fuel from bio-oil depends heavily on post pyrolysis treatment or upgradation due to the extent of requirement of deoxygenation and dehydrogenation (Hansen et al., 2020). The extent of upgradation of bio-oil from raw biomass can be decreased significantly through some pre-pyrolysis or during pyrolysis treatments (Kumar et al., 2020). The use of highly active and advanced catalyst is one of the most popular and widely accepted during pyrolysis treatment of biomass to obtain a higher grade bio-oil for producing transportation fuel. On the other, hand pre-pyrolysis treatment of biomass can be sub-grouped into physical, chemical and thermochemical processes. Grinding, densification or milling are the most popular types of physical or mechanical pretreatment of biomass which generally changes bulk density, particle size, crystallinity index or effective surface area (Jędrzejczyk et al., 2019). The main drawbacks of the physical or mechanical pretreatment of biomass is the high cost and limited improvements observed in the physicochemical properties of biomass when not combined with other biomass upgradation methods (Sundaram et al., 2017).

Chemical pretreatment of biomass mostly includes acids or alkali treatment in absence of heat. Chemical pretreatment of biomass can lead to changes in degree of polymerization, energy density, and biomass composition, concentration of metal ions and crystallinity of biomass. However, there are certain drawbacks associated with chemical pretreatment of biomass such as high maintenance cost, reactor corrosion and also the proper disposal of leachate which can be highly acidic or alkaline and may also contain some hazardous heavy metals. Chemical treatment of biomass also requires washing and drying post treatment of biomass which requires energy and time input making it an uneconomical biomass pretreatment process.

Thermochemical pretreatment of biomass is considered to be the most effective pretreatment process which is a combination of both heat and chemical reactions leading to substantial changes in physicochemical properties of the biomass. The various types of thermochemical pretreatment of biomass include hot water extraction, ammonia fibre expansion, and steam explosion, dry and wet torrefaction.

In wet torrefaction the raw biomass is treated with subcritical water or hot compressed water in the temperature range of 190-270 ^{o}C (He et al., 2018; Zhang et al., 2017). In wet torrefaction, other media can also be used such as hydrochloric acid, aqueous ammonia and acetic acid. However, as compared to dry torrefaction wet torrefaction is a complex process which requires specific reactor design made of special materials to with stand high pressure thus increasing input and running cost (Kumar et al., 2020). Wet torrefaction also produces waste water which may contain toxic metals coming from biomass during treatment thus creating disposal problem for waste water. Biomass undergoing wet torrefaction needs drying which requires both money and energy. Similarly other thermochemical pretreatment process such as hot water extraction, ammonia fibre expansion and steam explosion are complex processes which requires special and expensive reactors, higher maintenance and have limited effect on the physicochemical properties of the biomass. Hence, considering various drawbacks related to other pretreatment processes, dry torrefaction or simply known as torrefaction has been used in the present study for the pretreatment of biomass.

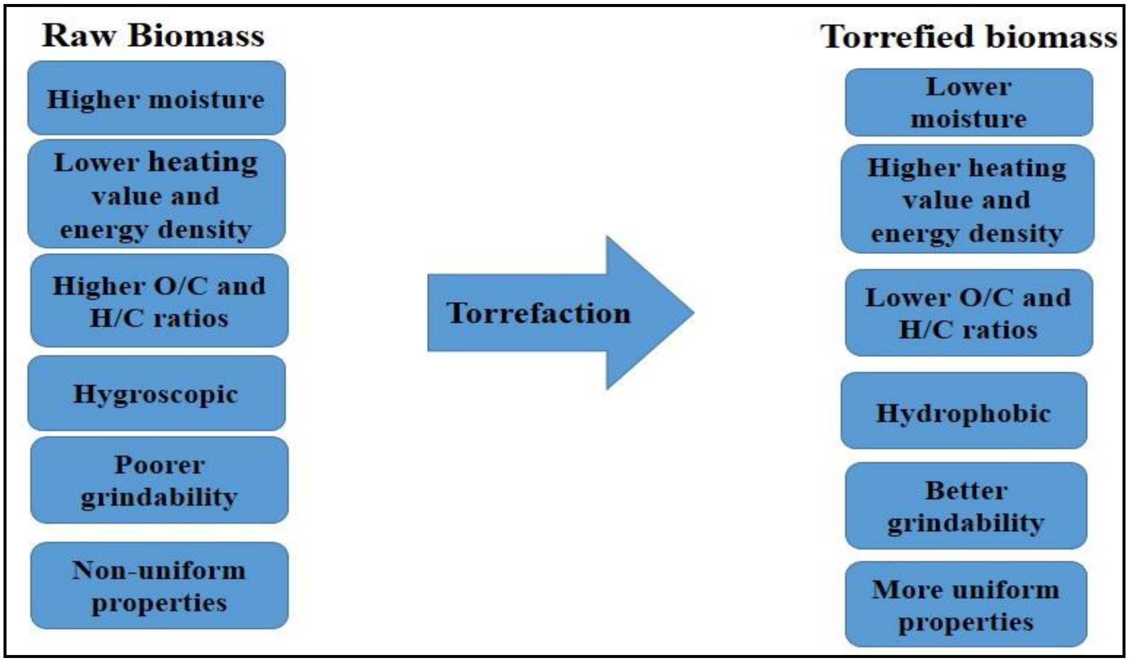

Fig. 1.2 Effect of torrefaction on raw biomass

Torrefaction is a thermochemical process generally operating at a lower heating rate with temperature range of 200-300°C in the absence of oxygen. The biomass undergoing torrefaction forms a charcoal-like carbonaceous material with better solid fuel properties such as reduced water content, better grindability, lower O/C ratio, improved logistics characteristics and high energy density as presented in Fig. 1.2. Based on the range of operating temperature torrefaction can be categorized into three groups as mild (200-235 ^{o}C), moderate (235-270^{o}C) and severe torrefaction (270-300 ^{o}C) (Chen et al., 2015; Singh et al., 2020). The biomass undergoing mild torrefaction witnesses small extent of hemicellulose degradation mainly due to dehydration of hydroxyl group and breakage of glycosidic bond (Chen et al., 2018). In moderate torrefaction the hemicellulose depolymerizes to a larger extent along with many bonds in the cellulose structure also degrades. Cellulose degrades during torrefaction mostly due to depolymerisation of free hydroxyl groups present in the glucose ring. Severe torrefaction on the other hand degrades almost all of the hemicellulose along with cellulose also degrading to a larger extent. Even though torrefaction produces biomass of much better qualities it still requires energy input hence, it becomes necessary to investigate the operating conditions and energy-exergy distribution of torrefaction process so that a cost effective pretreatment process can be established.

1.5 Pyrolysis

Pyrolysis is a thermochemical process which is generally operated above 350 ^{o}C and can go as high as 1300 ^{o}C in absence of oxygen (Akhtar and Saidina Amin, 2012; Bach et al., 2017; Biswas et al., 2017). Pyrolysis for biomass conversion is used to produce various fuels such as bio-oil, bio-char and noncondensable gases. Depending upon various operating conditions, pyrolysis can be divided into four sub-categories: slow, conventional, fast and flash pyrolysis. The occurrence of slow pyrolysis is at low temperature and heating rate for longer reaction or residence time while in flash pyrolysis the residence time happens to be for few seconds with very high heating rate. Generally, in flash pyrolysis the particle size needs to be very small to facilitate higher heat transfer due to increased biomass surface area. Fast pyrolysis occurs at a moderate temperature range with short residence time and heating rate greater than that of conventional pyrolysis but lesser than as in flash pyrolysis. Conventional pyrolysis operates at a moderate heating rate and temperature (350-650 ^{o}C) with residence time ranging between 0-30 minutes. Table 1.1 presents the operating parameters for the various types of pyrolysis along with their product objective. It can be observed from Table 1.1 that only conventional type of pyrolysis favours all three possible products that can be obtained from biomass. In the present study conventional pyrolysis has been used aiming to study the effect of torrefaction on all three products of pyrolysis and also, examine the energy-exergy distribution among different products to obtain optimized condition with higher efficiency and lesser energy input.

Table 1.1 Types of pyrolysis with operating parameters and favourable products (Basu, 2013; Bertero and Sedran, 2015)

Type of pyrolysis	Temperature (^{o}C)	Heating rate	Residence time	Favourable products
Slow	300-400	Very slow	Few hrs. to days	Bio-char
Conventional	350-650	20-100 ^{o}C/min	0-30 min	Bio-oil, bio-char and pyrolytic gas
Fast	450-650	10-200 ^{o}C/sec	0.5-5 sec	Bio-oil
Flash	800-1300	>1000 ^{o}C/sec	< 0.5 sec	Bio-oil

1.6 Contributions

The present research work focuses on torrefaction of biomass obtained from two different sources i.e. agricultural residue (pigeon pea stalk) and woody biomass (eucalyptus). The main drawbacks related to the use of raw biomass in co-combustion with coal and pyrolysis have been addressed. The present scope of work also covers the statistical analysis and the process optimization for both torrefaction and pyrolysis of torrefied biomass using response surface methodology (RSM). The solid fuel properties of torrefied pigeon pea stalk and eucalyptus have been compared to their respective raw biomass along with the physicochemical properties of by-products obtained during the pretreatment process. The present study includes various benefits and drawbacks associated with the pyrolysis of torrefied biomass in terms of bio-oil yield and their physicochemical properties. Furthermore, the study has also been extended towards energy and exergy analysis among various products obtained during torrefaction and pyrolysis of biomass along with the theoretical analysis of energy recuperation from by-products. The major objectives of the present thesis can be classified as follows:

1. Torrefaction of raw biomass obtained from two different sources (agricultural residue and woody biomass) for the possible generalization of operating conditions in comparison to other different biomass materials
2. Statistical analysis and process optimization of torrefaction for pigeon pea stalk and eucalyptus using response surface methodology (RSM)
3. Study the influence of operating conditions (temperature, residence time and heating rate) on various physicochemical properties of torrefied biomass related to co-combustion with coal and pyrolysis
4. Statistical analysis of operating parameters (temperature, residence time, heating rate and nitrogen sweeping rate) on bio-oil yield and process optimization of pyrolysis of torrefied biomass (obtained at the optimum condition) using RSM

5. Comparative study of physicochemical properties of bio-oil, pyrolytic gas and bio-char obtained from the pyrolysis of raw and torrefied biomass
6. Influence of operating temperature on the energy-exergy analysis of both torrefaction and pyrolysis
7. Theoretical analysis for improving the existing processes of torrefaction and pyrolysis by introducing energy recuperation from by-products leading to the development of an energy efficient system

1.7 Thesis Structure

The present study has been distributed into eight chapters, and brief outline of the respective chapters have been covered in this part. The Chapter 1 provides the introduction of biomass, its sources and brief coverage of torrefaction and pyrolysis. In the Chapter 2, a detailed literature review on distribution of biomass mainly in Indian perspective with especial emphasis on given agricultural residue and woody biomass has been presented. The different types of torrefaction with their benefits and drawbacks have also been discussed. The Chapter 2 also contains a detailed discussion on the influence of various operating parameters of torrefaction and pyrolysis on the yield of various products and their physicochemical properties. In the last section of the chapter, we have reviewed the work focussing on energy-exergy analysis for both torrefaction and pyrolysis. The Chapter 3 has been divided into two parts. In the first part of the Chapter 3, a detailed discussion on the experimental set-up along with the design and the statistical analysis of the torrefaction process using RSM for both pigeon pea stalk and eucalyptus has been carried out. In the second part of the Chapter 3, optimization of torrefaction process and its validation has been covered. The Chapter 4 covers the influence of operating parameters on the physicochemical properties of the torrefied biomass. In this chapter, the solid fuel properties of the torrefied biomass in the perspective of co-combustion with coal and pyrolysis has been discussed. The Chapter 4 also includes the estimation of kinetic parameters for the pyrolysis of raw and torrefied biomass using TG/DTG data for both pigeon pea stalk and eucalyptus.

The Chapter 5 presents the pyrolysis of both the torrefied biomass materials (using the optimum condition as obtained from the Chapter 3) along with the statistical analysis for the influence of operating parameters on the bio-oil yield and its optimization using RSM. The Chapter 5 also includes the comparative study for the physicochemical properties of pyrolysis products obtained from raw and torrefied biomass at the same operating conditions. The Chapter 6 has been divided into three parts, where first part includes the detailed information regarding various assumptions and thermodynamic equations used while calculating the energy-exergy values associated with the torrefaction and the pyrolysis process. The second part includes the detailed analysis of energy-exergy variation for torrefaction process with temperature variation and it also renders a theoretical analysis for reduction in energy required for the process through energy recuperation from by-products. Furthermore, the last part of the Chapter 6 includes the comparative study of the energy-exergy variation for the pyrolysis of raw and torrefied biomass at the same operating conditions.

The Chapter 7 summarizes the conclusions from the thesis and provides recommendations for future scope of work.