Chapter 2

Literature Review

2.1 Overview

This chapter presents a detailed literature review on biomass distribution and reasons behind the selection of pigeon pea stalk and eucalyptus for the present study. Further this chapter includes the torrefaction of biomass and the influence of various operating parameters on the qualitative and the quantitative analysis of torrefied biomass. Pyrolysis of biomass and factors affecting the bio-oil yield have been also discussed in the present chapter.

2.2 Biomass Distribution and Selection

Firstly, in order to predict the potential energy from biomass it becomes necessary to know the quantitative distribution of biomass from all possible biological sources. One such study was carried out by Bar-On et al. (Bar-On et al., 2018) where they estimated the total biomass distribution from all forms of life present on the planet Earth. They estimated that biomass carbon from all the sources could around 550 gigatonnes with plants contributing for the larger share of 450 gigatonnes. The other sources such as bacteria, fungi and animals contribute for 70, 12 and 2 gigatonnes of biomass carbon, respectively. It is worth mentioning that they predicted approximately 90% of the biomass carbon from bacteria could be present below the seafloor mostly resulting from a very slow metabolic activity which could have taken several months to thousands of year (Braun et al., 2017; Trembath-

Reichert et al., 2017). Biomass obtained from plants has the potential to produce a major chunk of fuels and chemicals requirement in a sustainable manner and thus subsequently phasing out the dependency on fossil fuels for these requirements (McCann et al., 2015). Agricultural and wood products along with their residues are the largest source of biomass obtained from plants. Here when we talk about biomass from plants it includes both cropland and forestland. In the view of diversifying the biomass sources and to avoid the food versus fuel debate, in the present study we have selected two different sources of biomass: agricultural residue and wood which have very limited utilization as source for food either for human being or cattle.

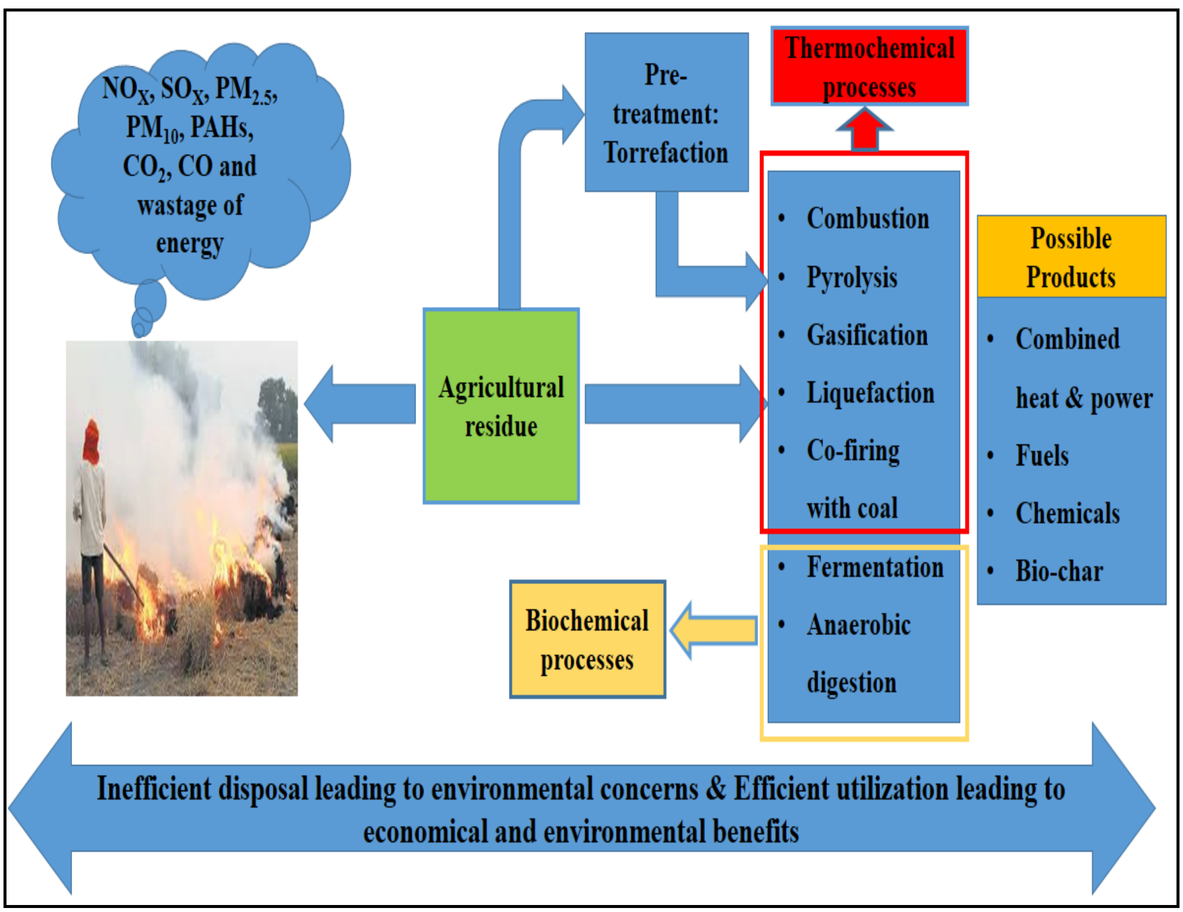

Fig. 2.1 Inefficient and efficient utilization of agricultural residue.

Global annual production of biomass in the form of agricultural residue stands at around 3700-5100 million metric tons (Bentsen et al., 2014; Wang et al., 2019). India and China are two major agricultural residue producing countries with an annual production of approximately 611 (Cardoen et al., 2015a) and 900 (Zong et al., 2015) million metric tons, respectively. However, it is worth mentioning here that only a fraction of annual agricultural residue can be utilized for power production due to its usage in other activities like composing, animal feed, domestic fuel, soil conservation etc. India has the annual production of around 213 million metric tons of surplus agricultural residue. India has the power potential of approximately 30 GW from its annual surplus agricultural residue (Singh, 2017). Fig. 2.1 presents the two routes for the disposal surplus agricultural residue and in recent times every year during the harvesting season Indian Sub-continent faces a very serious environmental problems due improper disposal of agricultural residue. In 2017 India alone accounted for 1.24 million deaths which were attributed to air pollution (Balakrishnan et al., 2019) and still every year India contributes maximum to the deaths happening worldwide due to air pollution.

In recent years the studies related to the energy conversion from agricultural residue have been limited mostly to popular agricultural residues such as sugarcane bagasse, rice husk and wheat straw leaving scope for the other equally important agricultural residues such as pigeon pea stalk, chickpea stalk and maze cobs. The studies have also shown that continuous adoption of rice and wheat over legume crops has led to a significant change in the nature of soil such as reduction in soil fertility, deterioration of soil health and anaerobic to aerobic environment (Gathala et al., 2011; Rai et al., 2019). These changes in the nature of soil has made the cultivation of wheat and rice as a highly input-intensive crops leading to high demand of irrigation and fertilizers. Pigeon pea which is a major legume crop especially for under developed and developing countries could be one of the most suitable alternative to rice in many regions (Singh et al., 2005). Pigeon pea is mostly cultivated in the subtropical regions of India, Pakistan, China, Zambia, Botswana, South Africa, and Ethiopia (Odeny Damaris, 2007). India being the largest producer and consumer of the pigeon pea in the world, which makes it the most suitable contender to efficiently utilize the crop residue obtained from pigeon pea. Approximately 2.9 tons/ha of residue is obtained from pigeon pea, making it one of the high residue producing crops (Cardoen et al., 2015a). Currently, most of the pigeon pea stalk obtained is used as a source for cooking fuel along with domestic ruminants and makes it underutilized biomass, fetching lower economic values to the farmers. It was quoted by D. Cardoen et al. (Cardoen et al., 2015a) in their study that residue to crop ratio (RCR) for Pigeon pea (4.10 ton/ton) was much higher as compared to wheat (2.07 ton/ton) and sugarcane (0.64 ton/ton). Also, about 84% of the crop residue produced from pigeon pea is utilized as a source of domestic fuel, which is much higher as compared to other conventional crops (Cardoen et al., 2015b), suggesting that no other primary application of this crop residue other than to generate heat.

Biomass derived from a partially or fully grown tree is considered as woody biomass. The main sources for woody biomass are forests, pulp and paper industries, wood scrap and wooden furniture industries. Depending upon the climatic and soil conditions different varieties of trees dominate in a particular region such as pine and oak trees are mostly found in the regions of North America, Europe and North-Asian countries where temperature remains mostly on the lower side with limited sun exposer. Similarly, eucalyptus is cultivated widely around the world in regions like Europe, Africa, North America, Australia, and Indian sub-continents. In India, more than 1 million hectares area is under eucalyptus plantation (Turnbull, 1999), and in some parts of north-west India, eucalyptus can produce 49.5-192.5 tons ha^{-1} total dry biomass (including root biomass) (Dagar et al., 2016). The eucalyptus tree is mainly utilized for pulp production along with furniture making, thus producing a large amount of wood residue which can be utilized for efficient energy production through pyrolysis. In Table 2.1 presents the properties of the raw biomass obtained from agricultural residue and woody biomass. Considering good availability, better growth rate and no food verses fuel conflict along with comparable properties (HHV, proximate and elemental analysis) as other popular feedstocks in their respective categories, both pigeon pea stalk and eucalyptus have been selected for biomass pre-treatment and biofuel generation in the present study.

Table 2.1 Properties of feedstock from various agricultural residue and woody biomass

Biomass	**References**	**Proximate analysis (wt%, dry basis)**			**Elemental analysis (wt%)**				**HHV (MJ/kg)**
		VM	**ASH**	**FC**	**C**	**H**	**N**	**O**	
Agricultural residue									
Pigeon pea stalk	(Surinder K. Katyal, 2000)	83.4	1.8	14.8	46.8	6.6	0.6	46.0	16.4
Rice straw	(Zhu et al., 2017)	75.4	10.0	14.6	44.1	6.1	0.7	49.1	16.6
Sugarcane bagasse	(Hassan et al., 2020)	80.6	6.7	12.7	42.1	5.6	0.3	52.0	19.0
Barley Straw	(Aqsha et al., 2017)	77.7	4.5	17.8	44.8	6.3	0.9	48	17.9

Corn stalk	(Chai et al., 2020)	77.8	6.3	15.9	46.4	7.0	0.3	46.3	16.1
Corn cob	(Azeez et al., 2010)	80.6	1.2	18.2	43.6	5.8	0.7	49.9	16.9
Wheat straw	(Zhang et al., 2020)	78.8	3.6	17.6	42.4	6.0	0.3	51.3	18.3
Jatropha residue	(Vichaphund et al., 2019)	73.5	6.7	19.8	48.0	6.9	5.8	39.3	19.3
Rapeseed cake	(David and Kopac, 2018)	75.4	7.5	17.1	45.9	6.2	6.8	41.1	25.4
Soybean straw	(Huang et al., 2016)	76.9	4.8	18.3	47.8	6.9	1.0	44.3	18.9
Cotton stalk	(Gupta et al., 2020)	74.0	6.5	19.5	39.6	6.0	0.4	47.5	15.8
Maize straw	(Wang et al., 2020)	78.4	5.5	16.2	45.3	5.9	0.8	48.0	18.2
Woody biomass									
Eucalyptus	(Xu et al., 2019)	88.0	1.9	10.1	47.3	5.8	1.2	45.7	19.3
Pine	(Pham et al., 2018)	82.1	0.3	17.6	54.8	5.7	0.1	39.4	21.8
Oak	(Kim et al., 2014)	87.1	0.7	12.2	46.1	6.4	0.2	47.3	19.9
Date tree	(Bharath et al., 2020)	82.0	8.5	9.5	51.9	6.7	-	41.6	12.7
Cottonwood tree	(Daniel et al., 2018)	71.6	2.7	25.7	48.5	6.0	0.7	43.0	17.3
Acacia nilotica	(Singh et al., 2020)	87.2	0.7	12.1	43.8	7.9	0.4	47.9	19.3

2.3 Torrefaction

Torrefaction was first performed in 1930's in France and was re-pioneered in 1980's by Bourgeois and Dot (Ciolkosz and Wallace, 2011; Niu et al., 2019; Prins et al., 2006b). Torrefaction is a pre-treatment process mainly done with an intent to enhance the fuel properties of the biomass by bringing physicochemical changes in its composition which mostly consists of hemicellulose, cellulose and lignin. Tumuluru et al. (Shankar Tumuluru et al., 2011) suggested that torrefaction of biomass can be divided into three zones: non-reactive drying, reactive drying and destructive drying zone each occurring during the temperature range of 50-150, 150-200 and 200-300 °C, respectively. In the non-reactive drying zone biomass undergoes only evaporation of surface moisture with non-occurrence of any chemical changes. The initial breaking of carbon and hydrogen bonds begins during the reactive drying zone along with the release of lipophilic compounds such as sterols, terpenes and unsaturated fatty acids. During the end of this zone depolymerisation and deformation of hemicellulose begins while in destructive drying zone complete destruction of hemicellulose happens with partial thermal degradation of cellulose and lignin. Similar trend was observed by Asadullah (Asadullah et al., 2014), where hemicellulose present in the palm kernel shell began to degrade at around 210 °C with complete decomposition taking place at around 280 °C. Significant thermal degradation of hemicellulose was also reported at 250 °C by Nam et al. (Nam and Capareda, 2015) and Chen et al. (Chen et al., 2012) for the torrefaction of cotton stalk and rice straw, respectively.

2.3.1 Influence of operating parameters on torrefaction

In the course of torrefaction operating parameters such as temperature, residence time, heating rate, particle size, and reactor design play an important role in the product distribution which can be broadly classified into solid residue (torrefied biomass), non-condensable gases (NCG) and liquid (condensable volatiles). Phanphanich et al. (Phanphanich and Mani, 2011) reported that during the torrefaction of woody biomass their solid and energy yield decreased from 89 to 52 wt% and 94% to 71 %, respectively, when the operating temperature increased from 225 to 300 °C at a constant residence time. Pimchuai et al. (Pimchuai et al., 2010) did a comparative study for the influence of temperature and residence time on solid and energy yield during the torrefaction of five different agricultural residue and reported that temperature had more significant effect as compared to residence time. Bridgeman et al. (Bridgeman et al., 2008) also reported similar trend where temperature had the most severe impact on product distribution and physicochemical properties of torrefied biomass as compared to residence time and biomass particle size where later had the least influence among all three operating parameters. Similarly, Sadaka et al. (Sadaka and Negi, 2009), and Huang et al. (Huang et al., 2019) also reported that temperature had the most severe effect followed by residence time while particle size had the least effect. Medic et al. (Medic et al., 2012) carried out a comparative study on the extent of influence of temperature and initial biomass moisture content where they reported that former had more profound effect on mass loss and energy yield.

During torrefaction particle size may have influence in the quality and quantity of the final product. Sabil et al. (Sabil et al., 2013) studied the effect of varying biomass particle size and temperature on mass and energy yield of torrefaction of palm kernel shell , palm mesocarp fiber and empty fruit bunches. They concluded that only temperature had the significant effect on the mass and energy yield while particle size had no appreciable effect on the quality and quantity of product. Uemura et al. (Uemura et al., 2015) also reported similar conclusion regarding the insignificant influence of varying biomass particle size on torrefaction products. However there were few studies like Chen et al. (Chen et al., 2014) and Medic et al. (Medic et al., 2012) who reported that biomass particle size also plays an important role during torrefaction due to its role in heat transfer mechanism. Heating rate is also one of the possible parameters which might be having significant role during distribution and quality of torrefaction products. Supramono et al. (Supramono et al., 2015) studied the effect of varying heating rate during the torrefaction of sugarcane bagasse. They observed that increasing the heating rate reduced the solid yield which was due to depolymerisation of cellulose rather than dehydration at higher heating rate. Finally they concluded that lower heating rate was desirable for torrefaction of biomass which favoured the formation of secondary char resulting in higher solid yield. Mundike et al. (Mundike et al., 2016) reported that variation of heating rate during torrefaction had influence on the HHV of the torrefied biomass of invasive alien plants such as Lantana camara *and* Mimosa pigra. Based on these discussions in the present study three operating parameters (temperature, residence time and heating rate) have been considered and rest other operating parameters have been kept constant.

2.3.2 Impact of torrefaction on product distribution and physicochemical properties

The solid yield during torrefaction decreases continuously with increase in severity due to release of moistures and volatiles. The solid yield during the torrefaction of rice husk as reported by Teh and Jamari (Teh and Jamari, 2016) decreased from 91.2 to 88.3 wt% and finally to 78.9 wt% when the torrefaction temperature increased from 220 to 250 and 280

°C, respectively. So and Eberhardt (So and Eberhardt, 2018) conducted the torrefaction of dry pine wood chips to understand the variation of solid yield due to varying temperature (230-260 °C) and residence time (120-180 min). They reported decrease in solid yield from 95.6 to 85.3 wt% and 93.0 to 82.8 wt% at 120 and 180 min residence time, respectively, when the operating temperature increased from 230-260 °C. Joshi et al. (Joshi et al., 2015a; Joshi et al., 2015b) in a series of their study on torrefaction of sugarcane bagasse and verge grass concluded that during the course of torrefaction in a particular temperature range there exist a quasi-equilibrium state during which the residence time had no or nominal effect on solid and energy yield. They also reported that energy yield of torrefied verge grass was higher as compared to torrefied sugarcane bagasse. Energy yield decreased with increase in severity due to significant mass loss resulting in low solid yield, however verge grass witnessed 25 % less energy yield drop as compared to sugarcane bagasse.

There torrefaction of sewage sludge was studied by Poudel et al. (Poudel et al., 2015a; Poudel et al., 2015b) where they observed that for severe torrefaction condition the HHV of solid residue decreased due to the breakdown of organic component present in the sewage sludge. They also reported that with increase in severity both solid and energy yield decreased due moisture loss and release of CO_2, CO, organics and acetic acid, respectively. Torrefaction of sugarcane bagasse, rice husk and peanut husk were carried out by Pimchuai et al. (Pimchuai et al., 2010) where solid yield, energy density and energy yield were in the range of 41-79 wt%, 1.1-1.7 and 55-98 %, respectively, when temperature and residence time were varied from 250-300 °C and 60-120 min, respectively.

2.4 Pyrolysis

Pyrolysis of biomass involves its heating in inert atmosphere at a predetermined heating rate to achieve the desired temperature (pyrolysis temperature) and holding it there for specific duration. The quality and quantity of pyrolysis products depends on factors such as pyrolysis temperature, residence time and heating rate. During pyrolysis initially the biomass produces mostly condensable gases and solid char where the some part of the condensable gas tends to break yielding non-condensable gases (CO_2, CO, CH_4 and H_2), along with char and bio-oil. These decompositions happens to some extent by gas phase homogeneous reaction and through solid-gas phase reactions of heterogeneous in nature. The homogeneous reactions of gas phase includes the thermal cracking of condensable part into smaller molecules producing non-condensable gases (pyrolytic gas) like CO_2 and CO. As discussed earlier that the pyrolysis of biomass involves the thermal decomposition of large molecules into smaller molecules and pyrolysis products mainly includes:

- Solid (bio-char)
- Liquid (bio-oil)
- Non-condensable pyrolytic gas which includes CO, CO_2, CH_4, H_2 and traces of C_2H_4, C_6H_6, etc.)

However, the relative yield of these pyrolysis products depend on factors such as biomass composition, pyrolysis temperature, heating rate, nitrogen sweeping rate and residence time.

2.4.1 Influence of operating parameters on pyrolysis

The operating parameters involved in the pyrolysis influences several chemical reactions which play an important role in the quality and quantity of end products obtained from the pyrolysis of biomass. The most influential operating parameters includes pyrolysis temperature, residence time, heating rate, nitrogen sweeping rate and residence time (Ben Hassen-Trabelsi et al., 2014; Demirbas, 2006; Guedes et al., 2018). The pyrolysis temperature plays an important role for the fact that this provides with the necessary heat required for the thermal decomposition of biomass. There have been numerous studies who have discussed the influence of pyrolysis temperature on the bio-oil yield with most of them showing higher bio-oil yield in the temperature range of 450-550 °C (Angın, 2013; Garg et al., 2016; Gerçel, 2002; Ly et al., 2016). Heating rate is also plays an important role in pyrolysis and several researchers like Trabelsi et al. (Ben Hassen-Trabelsi et al., 2014), Putun et al. (Pütün et al., 2008), Onay et al. (Onay and Mete Koçkar, 2004) and Sensoz et al. (Şensöz and Angın, 2008) that increasing the heating rate reduced the probability for the secondary cracking of the released volatiles and hence, this condition favours the formation of bio-oil. On the other side, few researchers have also observed that increasing the heating rate may decrease the bio-oil yield and this depends greatly on other factors such as biomass composition and pyrolysis temperature (Akhtar and Saidina Amin, 2012; Razuan et al., 2010).

Biomass particle size may also greatly affect the bio-oil yield during pyrolysis as biomass are very poor conductor of heat with may raise some issues related to the heat transfer mechanism (Akhtar and Saidina Amin, 2012). However, many researchers like Uzun et al

(Uzun et al., 2006), Encinar et al. (Encinar et al., 1998; Encinar et al., 2000) and Abnisa et al. (Abnisa and Wan Daud, 2014) have mentioned that the biomass particle size up to 2mm don't have any significant effect on the bio-oil yield. Also, very small particle size may have choking problem especially in a fixed bed reactor hence in the present study the particle size for the biomass has been kept between 0.7 to 1.2 mm. Residence time is an another important parameter for the decomposition of biomass and this represents the duration for which the biomass has been sustained at a specific temperature. This is a very important aspect especially in a fixed bed batch operations such as in the present study where biomass should be exposed sufficiently for achieving desired results. However, longer residence time can lead to secondary reactions such as gasification, carbonization and thermal cracking for the volatiles released during pyrolysis which results in to lower bio-oil yield (Bartoli et al., 2016; Guedes et al., 2018; Tsai et al., 2007). As mentioned earlier that the secondary cracking of the pyrolysis volatiles decreases the bio-oil yield and in this regard nitrogen sweeping rate also plays an important role. In the pyrolysis of biomass for the purging of volatiles, nitrogen is the most commonly used gas due to its inertness even at high temperature, easy availability and being economical as compared to other inert gases (helium and argon).

2.5 Response Surface Methodology (RSM)

Among various statistical techniques, RSM is a very popular multivariate technique available for the analytical optimization (Bezerra et al., 2008). There are several experimental designs like Box-Behnken, Doehlert design, central composite design (CCD), and three-level factorial, which can be used for statistical analysis. In the present study

CCD has been used to study the mutual influence of operating parameters during torrefaction and their pyrolysis.

Table 2.2 Process optimization for torrefaction and pyrolysis based using RSM

References	Biomass	Operating parameters and desired optimization	Optimum operating conditions
Torrefaction			
(Nam and Capareda, 2015)	Rice straw and cotton stalk	Temperature: 210-290 °C, residence time:20-60 min for maximum energy yield	210 °C and 20 min
(Chin et al., 2013)	Palm tree	Temperature: 200-300 °C, residence time: 15-45 min for maximum energy density with minimum weight loss	230 °C and 40 min
(Buratti et al., 2018)	Coffee industry residue	Temperature: 220-300 °C, residence time: 20-60 min, heating rate: 5-25 °C/min for maximum HHV with minimum weight loss	272 °C, 20 min and 5 °C/min
(Asadullah et al., 2014)	Palm kernel shell	Temperature: 200-320°C, residence time: 10-60 min, nitrogen sweeping rate: 100-400 mi/min for maximum solid yield	300 °C, 20 min and 300 ml/min
Pyrolysis			
(Mohammed et al., 2017)	Napier grass	Temperature:450-750 °C, heating rate:10-50 °C/min, nitrogen sweeping rate: 5-25 l/min for maximum bio-oil yield and minimum bio-char and pyrolytic gas	600 °C, 50 °C/min and 5 l/min
(Saikia et al., 2018)	Perennial grass	Temperature:300-550 °C, heating rate:20-60 °C/min, nitrogen sweeping rate: 70-250 ml/min for maximum bio-oil yield	550 °C, 20 min, 226 ml/min
(Dhanavath et al., 2019)	Neem pressed deed cake	Temperature: 450-575 °C, 30-60 min, 0.1-0.5 l/min for maximum bio-oil yield	512.5 °C, 60 min, 0.5 l/min

CCD was developed by Box and Wilson in 1951 (Box and Wilson, 1951) and consisted of full factorial or fractional factorial design, experimental point at a distance of α from its center with a central points. In the process of predicting the optimum condition RSM has a major advantage over other methods that it requires lesser number of experiments (Asadzadeh et al., 2018; Mohan Kumar et al., 2013). RSM also helps in simultaneous optimization of multiple factors in place of optimizing single factor (Ebadi et al., 2015). Table 2.2 illustrates some of the RSM based optimization processes for torrefaction and pyrolysis of biomass. However, no study has been found which deals with the statistical analysis for the pyrolysis of torrefied biomass (obtained at optimum condition).

2.6 Energy and exergy analysis

The thermomechanical analysis includes energy and exergy analysis. Exergy is a tool particularly beneficial in assessing and enhancing the thermochemical conversion (Ometto and Roma, 2010; Wang et al., 2016). First law of thermodynamics is the basis for energy analysis and thermal efficiency is the most important parameter of energy evaluation. However, it is well established that energy analysis can only present the amount of energy used rather than overall energy quality and its utilization in the process. In this regard, exergy analysis can help in understanding the amount of energy and quality of work at the same time. There were some studies regarding the energy and the exergy analysis of the biomass torrefaction. Prins et al. (Prins et al., 2006a) carried out theoretical studies regarding performance analysis of gasification system integrated with torrefaction process. Theoretical studies revealed that the overall performance and efficiency of the gasification system increased when torrefaction is introduced as a pretreatment process for biomass. Yen et al. (Yan et al., 2010) performed the mass and the energy balance for torrefaction of biomass (pine wood). Their study revealed that temperature had significant effect on product distribution, solid fuel characteristics and the reaction mechanism. Granados et al.

(Granados et al., 2014) performed the energy and exergy balance for torrefaction of different biomass at a constant temperature (250 ^{o}C), residence time (30 min) and heating rate (10 ^{o}C/min). Sawdust and rice husk were the best performing biomass during torrefaction based on energy yield and energetic balances, respectively. Wang et al. (Wang et al., 2016) studied the effect of pyrolysis temperature on the energy-exergy analysis for rice straw in a two stage fixed bed pyrolysis system and found that the energy and exergy value for the pyrolysis gas reaches maximum at 1000 °C.

2.7 Research gaps

From the available literature, it has been found that torrefaction as a pre-treatment process has a great potential to rectify some of the major drawbacks associated with the physicochemical properties of the raw biomass which can be utilized both as a solid fuel in combustion or for the production of bio-oil through pyrolysis. However, based on literature review the following research gaps have been identified.

- Study on the process optimization for the torrefaction of biomass based on maximization of both energy yield and HHV was not available

- Establishment for the generalization of optimum torrefaction condition which can be applicable to other biomass

- Study on the combustion indices of raw biomass were available, however, limited study was found for the combustion indices of torrefied biomass for co-combustion with coal and its variation with varying severity of torrefaction

- Detailed analysis of byproducts (liquid and torgas) obtained during the torrefaction of biomass in order to explore the potential for obtaining some value added products

- Energy and exergy analysis for all the possible products obtained from torrefaction process and theoretical analysis for energy recuperation from by-products to increase the efficiency of the torrefaction process

- Two-stage optimization for obtaining a high grade bio-oil from the torrefied biomass (1^{st} stage: torrefaction at the optimum condition and 2^{nd} stage: optimization for the pyrolysis of torrefied biomass obtained from stage-1)

- Comparative study of energy and exergy analysis for the pyrolysis of raw and torrefied biomass

Hence based on these research gaps the present thesis makes an attempt to fulfil these in subsequent chapters based both on a combination of statistical and experimental analysis.