Thermochemical behavior of pretreated biomass

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Abstract

Mankind has to provide a sustainable alternative to its energy related problems. Bioenergy is considered as one of the potential renewable energy resources and as a result bioenergy market is also expected to grow dramatically in future. However, logistic issues are of serious concern while considering biomass as an alternative to fossil fuel. It can be improved by introducing pretreated wood pellet.

The main objective of this thesis is to address thermochemical behaviour of steam exploded pretreated biomass. Additionally, process aspects of torrefaction were also considered in this thesis. Steam explosion (SE) was performed in a laboratory scale reactor using Salix wood chips. Afterwards, fuel and thermochemical aspects of SE residue were investigated. It was found that Steam explosion pretreatment improved both fuel and pellet quality. Pyrolysis of SE residue reveals that alerted biomass composition significantly affects its pyrolysis behaviour. Contribution from depolymerized components (hemicellulose, cellulose and lignin) of biomass was observed explicitly during pyrolysis. When devolatilization experiment was performed on pellet produced from SE residue, effect of those altered components was observed. In summary, pretreated biomass fuel characteristics is significantly different in comparison with untreated biomass. On the other hand, Process efficiency of torrefaction was found to be governed by the choice of appropriate operating conditions and the type of biomass.

Keywords: Biomass, Combustion, Pretreatment, Pyrolysis, Steam explosion, Torrefaction

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Above all, I dedicate this work to my parents.

List of appended publications

Supplement I

Biswas A K, Yang W, Blasiak W. Steam pretreatment of Salix to upgrade biomass fuel for wood pellet production. Fuel Processing Technology, 92 (9), 2011

The author performed the major part of the experimental works and contributed to the planning, evaluation and writing.

Supplement II

Biswas A K, Umeki K, Yang W, Blasiak W. Change of pyrolysis characteristics and structure of woody biomass due to steam explosion pretreatment. Fuel Processing Technology, Fuel Processing Technology, 92 (10), 2011

The author performed all of the experimental works and contributed to the planning, evaluation and writing.

Supplement III

Biswas A K, Yang W, Blasiak W. Devolatilization characteristics of steam explosion pretreated wood pellet. Fuel Processing Technology, Submitted, 2011

The author performed all experimental works, planning, evaluation and writing.

List of papers not included in this thesis

1. Umeki k, **Biswas A K**, Yang W, Blasiak W, and Yoshikawa K. Validity and Limitation of the shrinking core model for the apparent pyrolysis rate of wood particle, Fuel, Submitted,2011

2. **Biswas A K**, Umeki K, Yang W, Blasiak W. Change of pyrolysis characteristics to steam explosion pretreatment of biomass. International conference on Applied Energy, Perugia, Italy, 2011

3. Zhang L, Nehme W, **Biswas A K**, Yang W, and Blasiak W. Characterization of heat transfer and flame length in a semi-scale industrial furnace equipped with a hitac burners. Journal of Energy Institute, 83, 2010

4. **Biswas A K**, Zhang L, Nehme W, Swiderski A, and Yang W. Experimental investigation of nitrogen oxides emission and heat transfer for high temperature air combustion. 10th Conference on Energy for a Clean Environment. Lisbon, Portugal, 2009

5. Umeki K, **Biswas A K**, Yang W and Yoshikawa K. Pyrolysis of Large Wood Particle by High Temperature steam, Proceedings of the International Conference on Fluid and Thermal Energy Conversion , 7-10 December,2009, Tongyeong, South Korea.

Contents

Chapter 1

Introduction

This chapter addresses the global energy scenario and necessity of renewable energy. This discussion is further extended to bioenergy. An introduction to necessity and fundamentals of biomass pretreatment is also discussed.

1.1 World Energy Scenario

Fossil fuel powered the Industrial revolution and still remains preeminent in modern civilization. For instance, fossil fuels are the main propeller of China's and India's growth. It has helped to boost mankind's living standard by economic growth. On the other hand, economic growth is triggering energy consumption. In order to meet this increasing energy demand, increase of production is also necessary. Other side of this story reveals that the resources are also depleting due to over consumption. The reserve-to-production ratios are 43.2 years for oil, 57 years for natural gas, and 164 years for coal [1]. As a matter of fact, most of the major economies import their energy resources from the most unstable part of the world. This fact is not only reshaping the structure of geopolitics but also imposes insecurity of energy supply.

Mankind is not only consuming the natural reserve of fossil fuels but also warming up its climate. The average temperature of earth's atmosphere increased by 0.8 °C within last hundred years, two thirds of which was during the last three decades [2]. Scientific community, at least most them, attributed it to the release of greenhouse gases to atmosphere due to human activities such as deforestation and burning of fossil fuels. Predictions made by Intergovernmental Panel on Climate Change (IPCC) indicated a great challenge to humanity's sustainable existence. IPCC predicts that global temperature can be increased by 1.6-1.9 °C based on their lowest emission scenario [3]. Such Global warming will alter the global climate drastically which will eventually affect all living specie life cycle, including humans. If the atmosphere keeps getting warm, as the old joke has it, there will still be a planet but not for mankind.

Now humanity's greatest challenge is to provide sufficient energy to seven billion energy hungry people without burning the planet. The sustainable idea of using less energy is probably not a useful one unless economic growth stops (which is most improbable). Additionally, this spiral growth of energy consumption will eventually suppress most of the efficiency saving concept soon. Instead of being optimistic, as those energy technology prophets, it is time to focus on alternative energy sources which can ensure energy security, economic growth and sustainable future [4]. In this context, renewable energy technology provides a glimpse of hope to those optimists. The competition among different renewable resources (solar, wind, biomass) is turning

those technologies cheaper in comparison to each other. Although renewable technologies seem really promising, the task to find green alternative energy resources is challenged by the terms "Cheap" and "Reliable". Although many people are concerned about environmental benefits, the main motive behind any research, development and implementation is of course money. The question would be whether those technologies can really draw attention of those ambitious entrepreneurs who want to produce cheap products from cheap fuel like coal. Concepts such as green certificates or subsidies help those alternative resource initiatives but due to recent financial instability worldwide, especially in the western part of the world, this concept of subsidies is also a matter of concern for those entrepreneurs. In near future, all those alternative energy resources have to compete with fossil fuels with or without any support from government. Obviously research and development will boost those technologies to make them competitive to fossil fuel based technologies where lies the best hope for humanity [4].

1.2 Biomass and Bioenergy

Biomass is considered to be a promising alternative energy resource. All vegetation which captures pocket of sunlight through photosynthesis is named as biomass. While transforming sun's energy, biomass also captures carbon dioxide from the atmosphere. It's a gift of nature which helps through billions of years to transform and reshape the earth's atmosphere and facilitate life in this planet. The energy, available in plant cell, now interests mankind for the future supply of energy. Additionally, it is considered as carbon neutral. Carbon neutrality reveals that amount of carbon from the atmosphere can be stored in plant cell. Hence, biomass can be included to the concept of low carbon society with other renewable energies such as wind, hydro and solar. However, careless harvesting of plants does not make it sustainable. Unless efforts are made to ensure that equivalent amounts of biomass can replace the existing uses.

Biomass shares a significant portion of total energy consumption, around 11%, worldwide. Over two thirds of which is accounted in developing countries for cooking and heating whereas other part is used by developed countries in their industrial and residential sectors both for generation of electricity and heat [5]. Although biomass share in developed countries is less, countries which are rich in forestry sector, such as Finland and Sweden, share significant portion of their total energy consumption by bioenergy. In Sweden 28.6 % of total energy consumption was shared by bioenergy in 2007 [6]. Optimists often predict that the contribution of bioenergy, globally, can be lifted from 40 EJ/y to 100 -500 EJ/y in 2050 [5]. A study conducted by Richard TL [7] emphasized on the importance of logistics infrastructure of biofuels. Such enormous energy infrastructure of biofuels, to support 100-500 EJ/y, will likely to be supported by lignocellulosic feedstock. However, bulkier characteristics of lignocellulose feedstock imposed significant logistic challenges. For instance, energy required to grow and deliver lignocellulose biomass to the plant is around 7-26% of its energy value [7].According to the author, to satisfy the IEA target of 150 EJ/y from bioenergy, a total of more than 200 billion cubic meters (bcum)

has to be transported. Global volume of energy commodities were around 11.7 bcum in 2008. Thus, in 2050, transport volume of biomass would be significantly higher than the current capacity of the entire energy and agricultural commodity infrastructure if bulky biomass is transported [7]. However, feasibility of such huge infrastructure seems unforeseen. The bulk nature associated with biomass can be resolved by adopting pelletizing technology. Considering reported energy density of pellet, the total transported volume can be kept to 28 bcum. Additionally, adopting pretreatment technologies can further reduce the volume to 15 bcum [7]. Such feature of wood pellet drew attention to entrepreneurs and policy makers in late 90's. The first wood pellet was transported from Canada to Sweden in 1998, ever since overwhelm flourish of this industry was observed in Europe and North America. Sikkema R et al., [8] have documented approximately 650 pellet plants with production capacity of 10 million ton in 2009 in Europe. The future of pellet industry seems really promising such as European Biomass Association predicted that the consumption of 50 million ton will be reached in European countries by 2020 [9]. However, to hold such optimistic target, of course, politicians and stakeholders must concentrate on well targeted and strategic research both on technology and market development. Well targeted research with organized infrastructure can make bioenergy market to meet those optimistic predictions and more attractive to global community.

1.3 Pretreatment of Biomass

In recent times, biomass pretreatment, before pelletization, has been recognized as a potential key player in both logistic and handling on. Although conventional wood pellet minimize logistic problems of biomass, it holds some inferior characteristics both as fuel and pellet. As a fuel, use of biomass in combustion and gasification process involves technical difficulties such as low ash sintering temperature and low heating value [10-12]. Moreover, due to low bulk density the handling cost is considered to be crucial. Additionally, conventional pellet has lower hardness, lower specific weight, and high sensitivity to moisture. At the same time, wood should be screened to smaller particle size to have better pellet quality which imposes additional cost to the pellet producers [13]. Hence, improvement of wood pellet both in terms of fuel and pellet quality is indispensable.

In order to address those problems, biomass is required to be pretreated for improvement of its quality. Pretreatment of biomass not only improves its heat content but also facilitate others advantages: higher grindibiltiy, hydrophobicity. It is a promising method to pre-process low quality biomass into high energy density feedstock with consistent and uniform physical and chemical characteristics. Several pretreatment technologies have been introduced to improve the fuel quality such as torrefaction and steam explosion. In the following section, those technologies will be discussed briefly.

1.3.1 Steam Explosion (SE) Fundamentals

Steam explosion (SE) process involves heating of biomass under high pressure saturated steam with wide variety of residence time followed by explosive decompression. After steam pretreatment, biomass turns into dark brown color. Woody biomass consists of cell wall mainly with polysaccharides (cellulose and hemicelluloses) and aromatic polymers named lignin. SE pretreatment is known to bring adequate disruption of carbohydrate structure by releasing hemicelluloses into solution [14]. Additionally, both cellulose and lignin are also altered depending on the severity of the process [15, 16].

SE was mainly used for bio-ethanol production. Therefore, the considered optimal condition for SE pretreatment was based on the principal where least amount of sugar is lost due to dehydration with better accessibility to substrate. However, a compromise always has to be made while choosing process conditions due to conflict in outcomes depending on the process conditions. For instance, severe pretreatment conditions enhances better access to the substrate, however, decomposes sugars from both cellulose and hemicellulose. Sugar degradation during pretreatment is attributed to three distinct process named pyrolysis, oxidation and dehydration. When the pretreatment severity is lower, partial conversion of acid-liable polysaccharides into sugars govern the process [15]. Further increase of severity (milder condition) dehydration reaction becomes dominant causing loss of soluble sugars from plant polysaccharides. Severe pretreatment condition tends to initiate condensation reaction involving lignin, hemicellulose and cellulose derived product. Additionally, Lignin produced after severe pretreated condition is extensively modified. Steam explosion substrate usually exhibit hydrophobicity not only due to release of hydroxyl group from hemicellulose and cellulose molecules, but also deposition of condensate on the fibre [15].

Different types of wood and agricultural residue can be pretreated by SE process. It is usually regarded that young plants and hardwood species are more vulnerable to SE process. Traditionally, SE is performed in a batch reactor, however, continuous reactor can also be found. Chips of different size are used for SE pretreatment. The requirement of steam increases with the increase of chip size and moisture content in biomass. In summary, governing parameters for SE is pretreatment time, temperature, chip size, moisture content and type of wood.

1.3.2 Torrefaction Fundamentals

Torrefaction is a thermo-chemical treatment method with operating temperature varied from 200°C to 300°C under inert atmosphere. During torrefaction, biomass releases some of the highly reactive volatiles as vapors and resulting in clean and dark brown colored biomass with higher energy density [17]. Torrefaction process is governed by the thermal activation and depolymerization of hemicellulose molecules within the biomass [17]. According to Ciolkosz D et al.,[17]major reaction pathways for torrefaction include dehydration reactions to form water and solid 'torrefied biomass', deacetylization, and depolymerization, leading to the formation of

levoglucosan . Prins et al.,[18] investigated kinetics of torrefaction in the temperature range of 230-300°C. They observed a two-step mechanism in which first step is much faster in comparison with second step. They attributed the first step to the decomposition of hemicellulose while second step represents cellulose decomposition. Torrefaction at higher temperature conditions (>~270°C) is reported to initiate a greater degree of cellulose breakdown. Lignin has not been reported to experience substantial chemical alteration during torrefaction.

1.4 Research objectives and Outline of the thesis

The main objective of this thesis is to address different aspects of pretreated biomass when it is consider as a fuel for thermochemical process. Additionally, process aspects of torrefaction were also investigated. The outline of this thesis is illustrated in Figure 1. Chapter 3(Supplement I), describes fuel and pellet properties of SE residue. In Chapter 4 (Supplement II), pyrolysis characteristics of SE residue were examined and compared with untreated biomass. In Chapter 5(supplement III), thermochemical analysis of SE residue was further extended to devolatilization of SE pellet, considering end user application. Later on, process aspects of torrefaction were presented in Chapter 6. Finally, Chapter 7 addresses the concluding discussion.
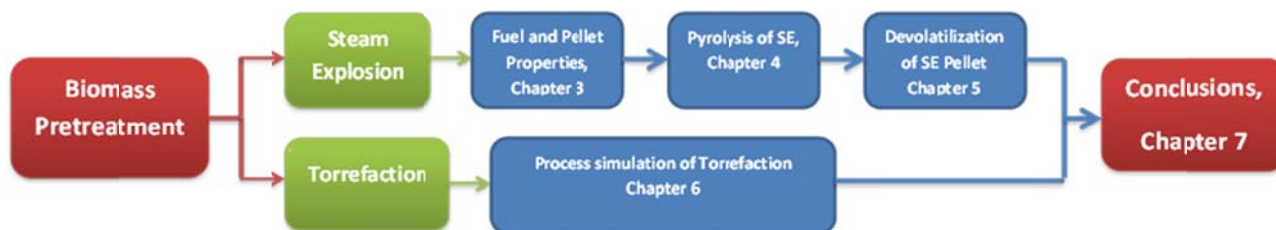

Fig.1: Outline of the thesis

Chapter 2

Steam Explosion Experiment

Steam explosion (SE) pretreatment is served to separate the main components of woody biomass. In general there is a noticeable gap in literature in terms of application of steam explosion process to upgrade biomass fuel for wood pellet production. In order to study the influence of steam explosion pretreatment on biomass as a fuel, SE was conducted on Salix wood chips by varying two major process parameters; temperature and time. This chapter discusses about the experimental procedure of SE.

2.1 Experimental

Short rotation willow (Salix) of chip size 2–10 mm was used for pretreatment experiment .Salix is mainly an energy crop which is cultivated in arable land. [19].The ultimate and proximate analysis of untreated biomass sample is shown in Table 1. The moisture content of fresh biomass was 46%. Wood was collected and chopped and stored in a plastic bag at 4 °C prior to experiment. SE experiments were performed using a laboratory scale reactor by varying two process parameters, temperature (T_p) and time (t). The detailed description of test facility and experimental procedure is explained elsewhere [19]. The steam used was in saturated condition. After pretreatment, biomass was separated from liquid and dried in air to reduce moisture content. Figure 1 shows the schematic presentation of SE experiments.

Table 1: Proximate and ultimate analysis of untreated biomass, dry basis

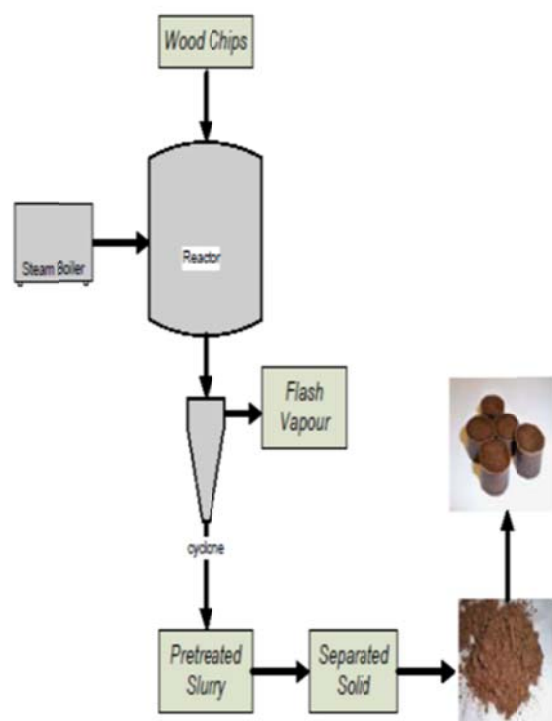|	[% db]
Proximate analysis	
Fixed carbon	16.4
Volatile	81.20
Ash	2.40
Ultimate analysis	
Carbon (C)	49.40
Hydrogen (H)	6.10
Oxygen (O)	41.80
Nitrogen (N)	0.29
Sulfur (S)	0.043

Fig. 1: Schematic diagram for assessment of the steam pretreatment

Chapter 3

Fuel and pellet properties of SE residue

This chapter intends to address the effect of SE pretreatment on fuel and pellet properties. This chapter is entirely based on **supplement I**. Four different SE experiments were considered to analyze impact of SE on fuel and pellet properties. Elementary quality and ash properties of the pretreated residue were investigated. Moreover, physical properties of the pellet, produced from the residue, were also investigated. Reduction in ash content especially in alkali metals was observed in steam treated residue. Pretreatment of biomass also enhanced carbon content and reduced oxygen amount in the fuel which enhanced the heating value of the fuel. Moreover, pretreatment significantly improved pellet density, impact resistance, and abrasive resistance of pellet. However, small degradation in ash fusion characteristics was observed as the severity of the process increased.

3.1 Introduction

Considering SE process for wood pellet production, it is important to focus on its fuel characteristics due to end use application. A number of studies on thermochemical conversion of SE residue, which had further gone through simultaneous saccharification and fermentation (SSF), showed promising features such no instability, low slagging tendency, very low emission of particulate and similar gaseous emission as other biomass [20-22]. However, application of steam explosion process in improvement of wood pellet is not often addressed. The objective of this chapter is to investigate the effect of steam explosion pretreatment on biomass as a fuel for thermal application as well as quality of wood pellet. In this context, SE residues were analyzed for fuel properties. Additionally, SE residue was used to make pellet and analyzed for physical property.

3.2 Experimental

3.2.1 Considered SE cases

Four different pretreatment conditions were chosen (see Table 1). In order to combine pretreatment parameters, temperature and time, severity factor (Ro) has been used [19,23]. It is defined by Eq. (1)

$$logRo = log\left[t\ exp\left(\frac{T-100}{14.75}\right)\right] \qquad (1)$$

Where t is the time in minutes and T is the temperature in °C.

Table 1: Pre-treatment conditions used in present study

Pretreatment	Temperature	Residence Time	10logRo
[-]	[°C]	[min]	[-]
A	220	6	4.31
B	228	6	4.54
C	220	12	4.61
D	228	12	4.84

3.2.2 Analytical method for steam treated residue

The calorific value of steam treated residue was measured according to CEN/TS 14918:2005. Ash, volatile and moisture content were measured according to CEN/TS 14775:2004, SS-ISO 562 and CEN/TS 14774:2004, respectively. Fixed carbon was calculated by difference. *C, H*, and *N* were evaluated according to CEN/TS 15104:2006. Oxygen content was calculated by difference. Sulphur content was measured by CENT/TS 15289:2006. Ash fusion characteristics were determined by CEN/TS 15370:2004. The mineral contents were measured according to EPA-mod 200.7 (ICP-AES), EPA-mod 200.8 (ICP-SMS) and SS 02 81 13 – 1. To examine the effect of SE pretreatment on mineral content and ash fusibility of biomass, samples from pretreatment case "C" and "D" were analysed.

The particle size distribution of steam treated residue was examined on air dried sample. The moisture content of the sample was around 7.5 % .Three different sieve sizes (1 mm, 1.5 mm and 3.5 mm) were used to analyse the particle size distribution. A sieve shaker with both horizontal and vertical motion was used for this analysis.

3.2.3 Physical properties of pellet

For pelletizing of steam treated residue, air dried materials were moisture conditioned to 8% by adding calculated amount of water. The moisture conditioned material was kept at 4°C for 72

hours in a plastic bag to have uniform moisture distribution. Prior to pelletizing, the material was screened through a 2.5 mm sieve to separate bigger particles. A 16 mm diameter of cylindrical mold was used to make pellet. Pelletizing was performed in a piston press at room temperature. Pellet properties were measured 24 hours after the log was made.

The abrasive resistance of pellet was measured by adopting so called tumbler test for coal (ASTM standard method D441-86). In this test three logs were placed in a porcelain jar and subjected to rotation at 70 rpm for 40 minutes. To increase harshness of this test, equal number of hexagonal nut of size 8 mm was kept with the pellet batch during the test. The weight of each log was measured before and after the tumbling test. The average loss of mass for each pellet batch shows as an indicator for abrasive resistance. The impact resistance test was performed by adopting the methodology of Lindley and Vossoughi [24]. In this test, logs from each case were dropped from a height of 1m for 10 times on a concrete floor and the change in mass was recorded. The percentage of mass loss shows as an indication of impact resistance.

3.3 Results and discussion

3.3.1 Fuel characteristics

3.3.1.1 Effect of steam pretreatment on elemental compositions

Biomass fuel property was significantly altered by steam pretreatment. Fixed carbon content was increased, whereas volatile content was reduced in pretreated residue. Proximate and ultimate analysis of both untreated and steam treated biomass is shown in Table 2.

Table 2: Proximate and ultimate analysis of untreated and steam treated biomass, dry basis

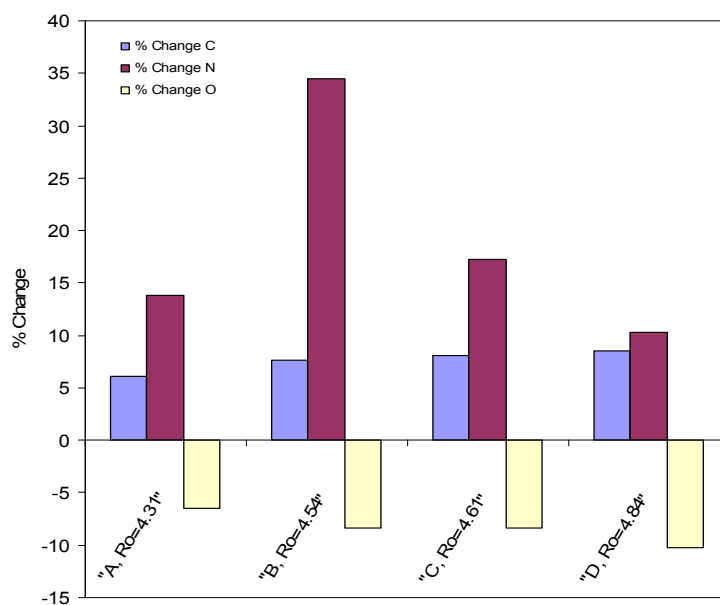|	Untreated Biomass	Pretreatment A	Pretreatment B	Pretreatment C	Pretreatment D
	[% db]	[% db]	[% db]	[% db]	[% db]
Proximate analysis					
Fixed carbon	16.4	17.8	19.3	18.7	20.3
Volatile	81.2	80.2	78.7	79.5	77.2
Ash	2.4	2	2	1.8	2.5
Ultimate analysis					
Carbon (C)	49.4	52.4	53.2	53.4	53.6
Hydrogen (H)	6.1	6.1	6.1	6.1	6
Oxygen (O)	41.8	39.1	38.3	38.3	37.5
Nitrogen (N)	0.29	0.33	0.39	0.34	0.32
Sulfur (S)	0.043	0.038	0.038	0.04	0.038

Fig.1: Percentage change in C, O, and N as a result of steam treatment as compared to untreated biomass
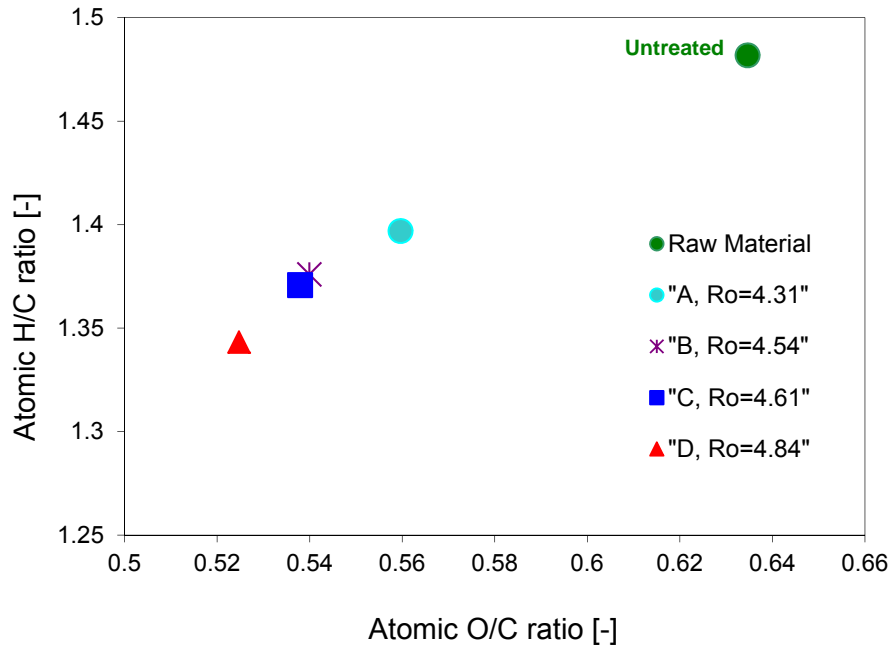
Fig. 2: Van krevelen diagram for untreated and steam treated biomass

Both pretreatment parameters, temperature and time, has noticeable impact on fixed carbon and volatiles. Experiment at 228°C (i.e. pretreatment case B and D), showed greater amount of fixed carbon and less volatile as compared to experiment at 220 °C (i.e. pretreatment case A and C). Similar behaviour was observed when pretreatment time was varied. At certain temperature (i.e. 220°C), increase in pretreatment reaction time evidently increases fixed carbon content and decrease volatiles. The major source of volatiles in biomass is cellulose. Moreover, hemicellulose and lignin contribute largely to the formation of char [25]. Therefore, reduced volatile content and increased fixed carbon at higher pretreatment temperature and time is attributed mainly to percentage increase of lignin in biomass due to removal of hemicelluloses and cellulose. Similar, observation was also made by other researchers [14,25]. Alteration of biomass fuel characteristics became evident while observing the ultimate analysis of the sample. When biomass was exposed to steam treatment, rise in carbon content was observed, whilst almost no change was observed in the hydrogen concentration (see Table 2). Fig. 1 shows the percentage changes in carbon, nitrogen and oxygen as compared to untreated biomass. Carbon content increased with the increase in severity (Ro) of the process. Maximum increase in carbon content can be observed for steam treated case "D". On the other hand, oxygen concentration was significantly altered in steam treated residue. For severity factor of 4.84 (case D), the recorded decrease in oxygen concentration was 10.28 %, whilst 6.45 % reduction was achieved for severity factor of 4.31(Case A) in comparison with untreated biomass (see Fig. 1).

Furthermore, nitrogen content in hydrolysis residue was increased drastically. Approximately, 10 to 35 % increase in nitrogen content was observed in pretreated residues. These compositional changes in biomass were reflected evidently on Van Kreven diagram. A plot of the Van Kreven diagram shows that both atomic ratios decreased by implementation of steam pretreatment (Fig. 2). For milder pretreatment condition (Case "A"), the elementary composition remained in the peat region of Van Krevelen diagram. Furthermore, with increased severity factor of the process, treated biomass showed a tendency of shifting towards lignite region in Van Krevelen diagram. Therefore, during steam pretreated biomass loses more oxygen as compared to carbon. According to Ramos [15], during pretreatment, both cellulose and hemicellulose are degraded and principle reactions are the hydrolysis of hemicellulose and rejection of polysaccharides as dehydration by-product, and it causes further increase in relative amount of lignin components. As a result, increase in carbon content was observed for pretreated residue. Lignin is considered as one of major source of nitrogen in biomass [27].Therefore, relative increase in nitrogen content for pretreatment case "A" and "B" is attributed to the increase of lignin fraction. Further increase in pretreatment severity (Case "C" and "D") may lead to extensive hydrolysis of lignin causing decrease in nitrogen content in comparison with case "A" and "B". On the other hand, condensation reaction between hemicellulose degraded product and lignin, at severe condition, promote relative amount of carbon in biomass.

3.3.1.2 Higher heating value and Energy Yield

Alteration of elemental composition of biomass due to steam pretreatment was reflected on the heating value of residue. Fig. 3a shows the relationship between higher heating value and pretreatment severity. Heating value of pretreated residue showed a clear relationship with pretreatment severity factor (Ro). Higher heating value was calculated by following formula.

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.0151N - 0.1034O - 0.0211ASH$$

To observe overall energy yield, the dry ash free mass and energy yields were calculated by following formulas

$$\text{Mass Yield}, \ Y_{mass}(\%) = \left(\frac{m_{product}}{m_{feed}} \right)_{daf} \times 100$$

$$\text{Energy Yield}, \ Y_{energy}(\%) = Y_{mass} \times \left(\frac{HHV_{product}}{HHV_{feed}} \right)_{daf}$$

The percentage mass and energy yield for steam treated residue with severity factor is shown in Fig. 3b. For severity factor of 4.31, the mass and energy yield remained high among those investigating conditions. However, after severity factor of 4.31, reduction in mass yield was

reflected on energy yield. Therefore, higher severity of the process reduces energy yield due to excessive mass loss during SE process.
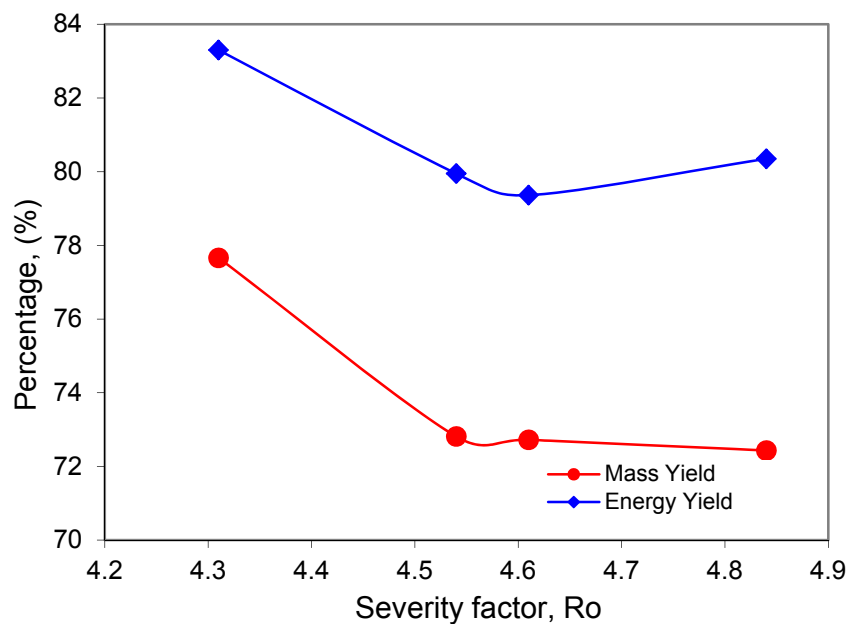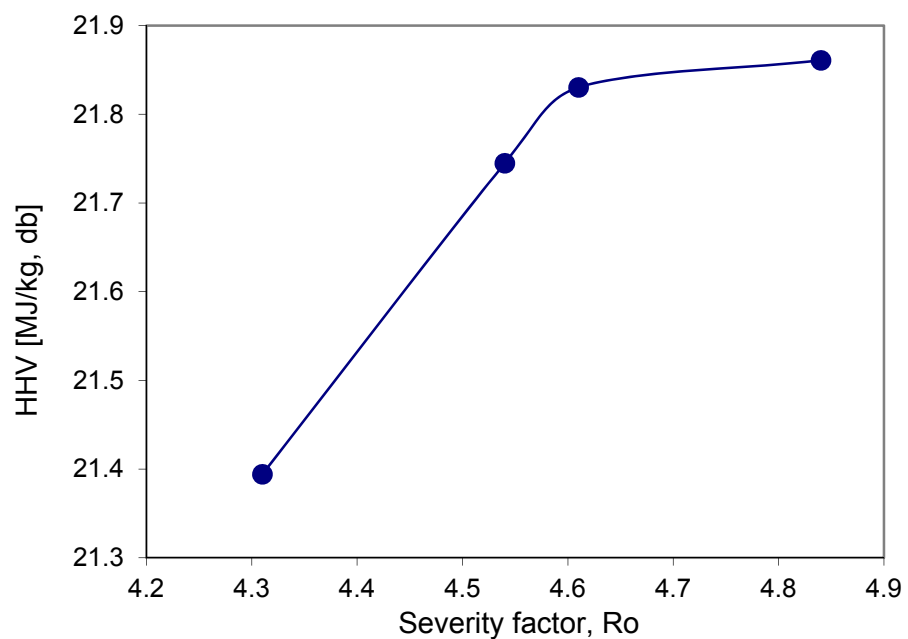

Fig. 3: a) Higher heating value b) Mass and Energy yield for steam treated residue, along severity factor

3.3.2 Ash characteristics

3.3.2.1 Total ash content, mineral mater, phosphorus and sulfur:

Reduction in ash amount was observed in hydrolysis residue. Fig. 4 shows total amount of ash in biomass with respect to severity factor (*Ro*) of the process. Total amount of ash was calculated by following formula:

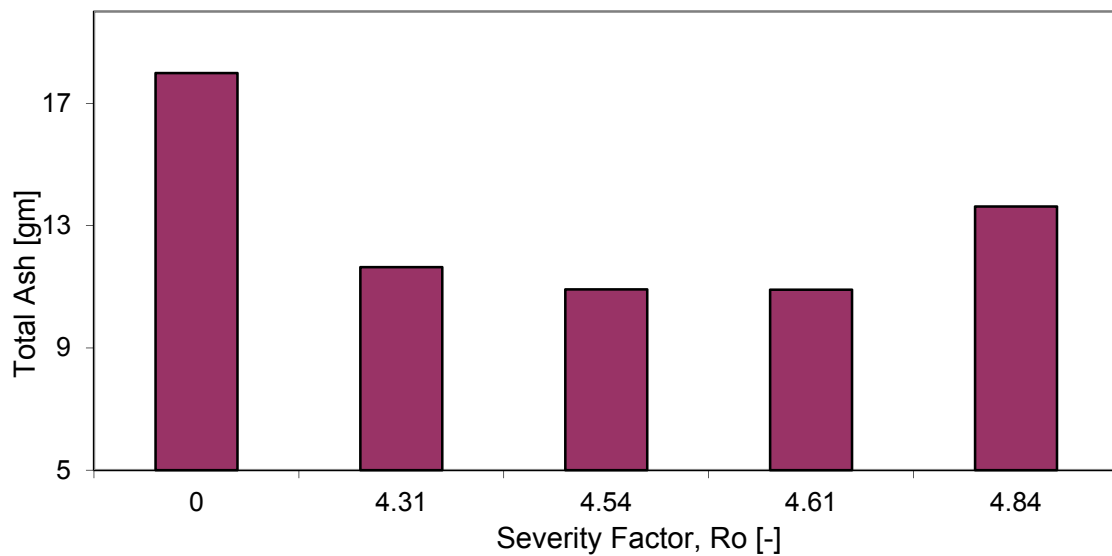$$Total\ Ash = \frac{mass\ yield(db) * \%Ash\ in\ biomass}{100}$$

Fig. 4: Total ash amount in the untreated (Ro=0) and pretreated biomass, presented with respect to severity factor (dry basis)

For sake of simplicity, severity factor (*Ro*) for untreated biomass was considered as zero. From severity factor of 4.31 to 4.61, total ash amount in pretreated residue was reduced almost monotonically. Reduction in ash content in hydrolysis residue was also observed by Öhman and coworkers [20]. Furthermore, Jenkins and coworkers [28] also identified that water leached biomass showed significant reduction in ash concentration. In steam explosion pretreatment, lignocelluloses structure of biomass is greatly disrupted. Hence, mineral matter present in biomass released to soluble liquid of the process. Therefore, reduction in ash content can be considered as the combined effect of both disrupted cell structure and the fact of water leaching process. In general, reduction in total ash content can be achieved by implementation of steam treatment as mineral matter dissolves in soluble liquid during the process.

To examine the effect of SE pretreatment on different mineral matter, detailed analysis of ash was performed on two extreme pretreatment cases (i.e. Case C and D). Pretreatment is striking in the extent at which potassium (K) was removed from biomass .The K content in the untreated biomass was found as 1830 mg/Kg db and measured K content for steam treated case "C" and "D" were 961 mg/Kg db and 706 mg/Kg db, respectively. Sodium (Na) content was also reduced in pretreated residue. The recorded Na content was 86.8 and 109 mg/ kg db for pretreated case "C" and "D", whereas untreated biomass had amount of 237 mg/kg db. For biomass, the major alkali metal in concern is potassium. Potassium is important in context of ash melting behavior [29]. Moreover, increased potassium concentration enhances aerosol formation during combustion, thus results in fouling in boiler. Therefore, reduction in alkali metal is foremost desirable. From present observation, it is obvious that reduction in alkali metal content in biomass can be achieved through implementation of steam explosion pretreatment. Sulfur content also reduced after pretreatment. From a concentration of 0.043 % S in untreated biomass, after pretreatment it reduced to 0.038~0.04 % (see Table 2). Although the difference is not considerably noticeable, but it reveals that SE treatment can be used for high sulfur containing biomass such as straw. The impact of steam pretreatment on phosphorus content of biomass is still not evident. For a concentration of 774 mg/Kg db of P in fresh biomass, steam treated residue showed 833 and 538 mg/kg db for steam treatment case "C" and "D", respectively.
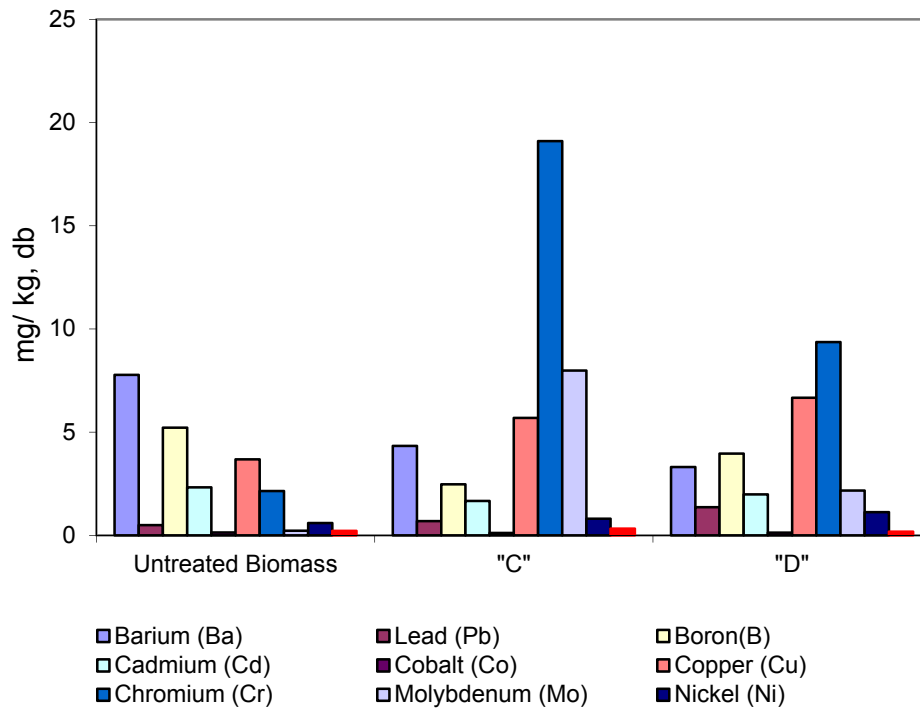

Fig. 5: Heavy metal composition in untreated and pretreated biomass

Reduction in heavy metal content was also observed in pretreated residue. Detailed analysis of heavy metal components of pretreatment conditions "C" and "D" is shown in Fig 5. Total amount of heavy metals in untreated biomass was 124.77 mg/ Kg db. On the other hand, steam treated residue showed 93.95 and 86.52 mg/Kg db for pretreatment case "C" and "D", respectively. Some of the heavy metal elements (Ba, B, Co, Zn, Cd) showed significant drop on concentration after pretreatment. However, the concentration of (Cu, Cr , Pb, Mo, Ni) exhibits small increase in concentration after pretreatment. Heavy metals have strong impact on the ash quality as well as on particulate emission. As a result, considering ecological reasons, the amount of heavy metals should be reduced in wood.

Upon inspection of the above observations, it should be pointed out that steam explosion pretreatment seems promising in reduction of alkali and heavy metal content of biomass.

3.3.2.2 Ash fusibility characteristics

Increase in steam pretreatment temperature from 220 to 228 °C showed detrimental effect on ash fusibility of biomass. Table 3 shows the ash fusion characteristics for both untreated and steam treated biomass samples. The measured shrinkage temperature (ST) of untreated biomass was 1160 °C. In comparison to untreated biomass, the shrinkage temperatures (ST) of steam treated samples were reduced by 110 °C and 160 °C for pretreated case C and D, respectively. A slight drop in deformation, hemisphere and flow temperature was also observed for severe steam treated condition (case D, R_o=4.84). However, Öhman et.al., and Blunk et. al., observed opposite behavior for hardwood samples [20, 22]. To understand this deviation in ash fusion behavior, available ash fusion indices is used. A number of analytical approaches have been considered to predict sintering tendency of ash [30]. One of those approaches includes the ratio of basic and acidic oxides as an index [31].

$$\text{Slagging Index, } SI = \left(\frac{CaO + MgO + Na_2O + K_2O + Fe_2O_3}{SiO_2 + Al_2O_3 + TiO_2} \right)$$

Table 3: Ash fusion characteristics both for untreated and steam treated biomass

Fusion State	Untreated material	Pretreatment C	Pretreatment D
[-]	[°C]	[°C]	[°C]
Shrinkage Temperature, ST	1160	1050	1000
Deformation Temperature, DT	>1500	>1500	1410
Hemisphere Temperature, HT	>1500	>1500	1440
Flow Temperature, FT	>1500	>1500	1470

In present investigation, slagging index (SI) was found to be 14.28 and 14.45 for pretreatment condition "C" and "D", respectively. In general, basic oxide compounds lower the melting

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temperature and acidic compounds increase it [32]. Therefore, at severe condition of steam pretreatment, the basic oxide components were increased as compared to acidic components which in turn reduce the ash fusibility of biomass.

3.3.3 Physical properties of pellet

3.3.3.1 Pellet Density

High density wood pellet was obtained from steam treated residue. Fig. 6 shows the effect of applied pressure on the density of the pellet. It is obvious that the density of the pellet increased with the increase of pressure. At certain pressure, pellet batch with higher severity factor (Ro) showed higher density. This phenomenon can be explained by considering particle size distribution of steam treated residue. Particle size distribution of air dried steam treated material is shown in Fig. 7. Process with higher severity factor tends to produce more fines. For instance, case "D" produces around 40 weight percentage of particles which have size less than 1.5 mm. On the other hand, process with lower severity (case "A") produces around 14 weight percentage of particle which is less than 1.5mm. Therefore, during pelletization, particle per unit volume is increased and porosity of the pellet is decreased which results in increase of pellet density.
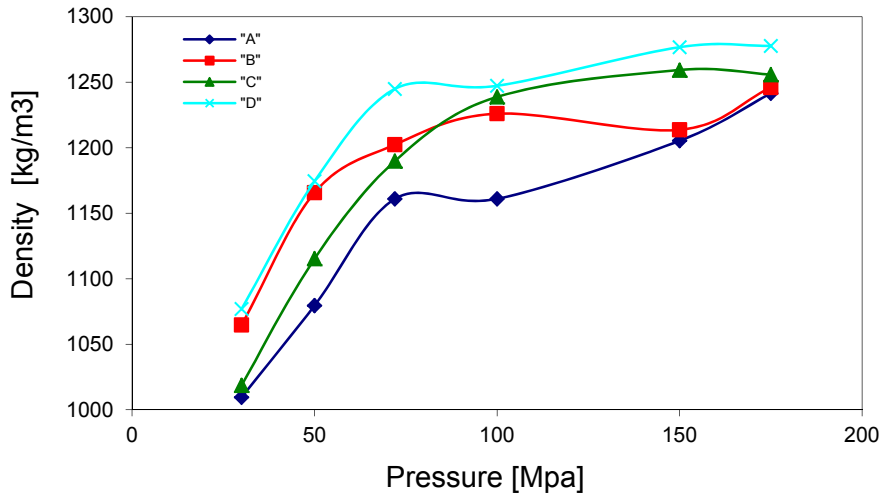

Fig. 6: variation of dry density of pellet with compaction pressure for pellet made from four different pretreatment conditions after 24hrs
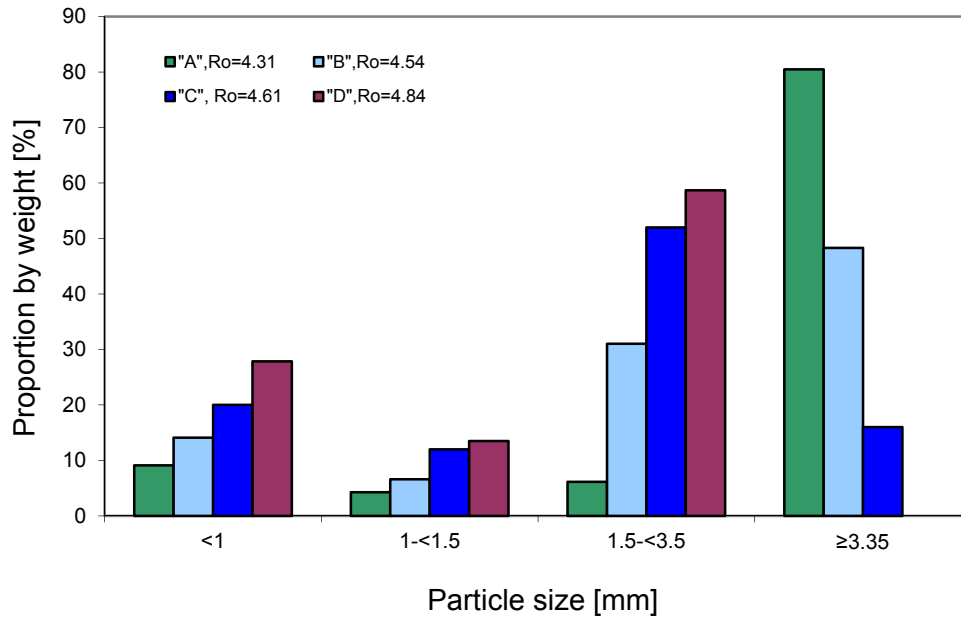
19

Fig. 7: Steam treated material's Particle size distribution

Beyond applied pressure of 72 Mpa, steam treated pellet (case "D") did not show drastic difference in pellet density. Pellet density remained around 1250 to 1267 kg/m^3. In general, the applied pressure in commercial pellet mill stays around 100 Mpa and pellet density of 1000 ~ 1100 kg/m^3. Therefore, wood pellet from SE pretreatment showed significant rise in pellet density even at lower applied pressure.

3.3.3.2 Impact and abrasive resistance

Physical properties of wood pellet were greatly improved due to steam pretreatment. Table 4 shows impact and abrasive resistance for different pellet batch produced from pretreated residue. The impact resistance test reveals that all fuel pellets showed consistent behaviour. Test had been repeated for 5 times for each pellet batch, no significant difference was observed. In accordance with the results from impact resistance test, abrasive resistance of each pellet batch also showed higher resistance. Previously, abrasive resistance has been correlated to particle size distribution in pellet [33]. Higher amount of fines in the pellet is considered to create more durable pellet. The study conducted by Bergström and co-workers [13] showed that pellet with finer particle size distribution had abrasive resistance of 98.8%.Although steam explosion process produces higher amount of fines, no real statement on particle size distribution was observed from the tumbling test. However, this phenomenon can be explained by considering the structural change of wood fibber due to steam pretreatment. Angles and co-workers [23] observed that at severe pretreatment condition, lignin in wood cell comes out of the fibre. Therefore, during pelletizing

process lignin melts on the surface of the pellet and create hard layer around it. In comparison with conventional pellet, it is evident that steam treatment significantly enhances durability of pellet by providing almost 100% durable pellet.

Table 4: Pellet mechanical properties

Pellet from pretreatment	Adjusted Density	Abrasive Resistance	Impact Resistance
[-]	[kg/m3]	[%]	[%]
A	1201	99.8	99.9
B	1234	99.9	99.9
C	1231	100	99.9
D	1240	99.8	99.9

Chapter 4

Pyrolysis characteristics steam exploded residue

This chapter investigates changes in biomass structure due to implication of steam explosion process by its pyrolysis behavior/characteristics. This chapter is entirely based on **supplement II**. Pyrolysis characteristic was examined by thermogravimetric analyzer (TGA) at heating rate of 10 °C/min. Both pyrolysis characteristics and structure of biomass were altered due to SE pretreatment. Hemicellulose decomposition region shifted to low temperature range due to the depolymerization caused by SE pretreatment. The peak intensities of cellulose decreased at mild pretreatment condition while it increased at severe conditions. Lignin reactivity also increased due to SE pretreatment. However, severe pretreatment condition resulted in reduction of lignin reactivity due to condensation and re-polymerization reactions. In summary, higher pretreatment temperature provided more active biomass compared with milder pretreatment conditions.

4.1 Introduction

Pyrolysis is one of the major conversion steps during thermochemical conversion of solid fuels. Therefore, it is important to focus on its pyrolysis characteristics since variation in main components of biomass has significant effect on its reaction behavior. Despite a number of studies on thermochemical behavior of steam pretreated residue has been conducted, most of them were performed on the residue which had gone through simultaneous saccharification and fermentation (SSF) [20-22]. In such studies, lignocelluloses structure was further modified due to SSF. A limited number of studies have been previously reported considering pyrolysis of SE residue [14,34-35]. Xu et al. [34] observed increase in char yield after pyrolysis for steam pretreated wool fiber residue. They associated this observation with removal of loose substances of biomass during steam explosion. Deepa et al. [35] observed slight change in degradation temperature of hemicellulose in SE pretreated banana fiber residue which was attributed to the presence of trace quantity of hemicellulose. Negro et al. [14] observed shift in lignin peak towards lower temperature for severe pretreated residue in comparison with the mildest condition. They suggested development of thermolabile chemical bonds in lignin when severity of pretreatment was high. Although those studies provide pyrolysis behavior of SE residue, no study was found which investigated detailed effect of process parameters of steam explosion (i.e. pretreatment temperature and time) on the pyrolysis characteristics of SE residue.

The aim is to observe the effect of SE conditions on the reactivity of woody biomass during pyrolysis process. Structural changes of biomass were examined to address the reason why reactivity changed due to SE. Salix chips were used as samples for SE pretreatment. Thereafter, thermogravimetric analysis with raw sample and pretreated residues was performed under pure nitrogen atmosphere.

4.2 Experimental

Three pretreatment temperatures were chosen: 205, 220 and 228 °C. For pretreatment temperature of 205°C and 220 °C, pretreatment time was chosen as 6 min, 9 min and 12 min. For 228 °C, pretreatment time was set as 6 min and 12 min.

Pyrolysis of SE residue was performed in a thermogravimetric analyzer (TG, PerkinElmer) under nitrogen atmosphere. The nitrogen flow rate was kept at around 300 ml min^{-1} at standard state. Prior to the experiments, samples were ground to a particle size less than 0.125 mm in order to minimize intra-particle heat and mass transfer effect on the pyrolysis behavior. A sample weight of around 5 mg was used in every occasion and placed in a crucible. Initially, the biomass was heated to 100 °C and kept for at least half an hour under the nitrogen atmosphere to remove all the moisture content from biomass. Afterwards, biomass sample was heated from 100 °C to 750 °C at a heating rate of 10 °C /min. The residual mass and sample temperature were recorded every 4 seconds. Residual mass ratio, derivation of thermogravimetry (DTG) and conversion ratio are represented by following equation:

$$\text{Residual mass ratio,} \quad \alpha = \frac{m_i}{m_o} \tag{1}$$

$$\text{Derivation of thermogravimetry} \quad DTG = \frac{d\alpha}{dT} \tag{2}$$

$$\text{Conversion ratio,} \quad X = \frac{m_0 - m_i}{m_0 - m_\infty} \tag{3}$$

X-Ray diffractometry (XRD) of both untreated and pretreated biomass was carried out using a diffractometer (Siemens, D 5000), with monochromatic Cu Kα radiation (λ=0.154180 nm), generated at 35 kV and 40 mA. The scanning was performed as follows: Scattering angle, 2θ=10-30°; step in 2θ of $\Delta 2\theta = 0.02°$.

4.3 Results and Discussions

4.3.1 Effect of SE condition on the reactivity of residue

In order to have comprehensive view of change in reactivity by pretreatment of biomass, pyrolysis temperatures at different conversion ratios were examined. In previous studies [37], temperature at 50% (T_{50}) of conversion ratio was used to describe pyrolysis reactivity where lower T_{50} temperature indicates faster decomposition of the biomass. In this study, pyrolysis temperatures at three different conversion ratios, 10 %, 50 %, and 90%, were used as listed in Table 1 with their corresponding weight loss rate.

Table 1: Pyrolysis Temperature and weight loss at three different conversion ratios, 10%, 50%, and 90%

Pretreatment conditions		Conversion ratio (%)					
Temperature	Time	10		50		90	
		Temp [°C]	DTG [wt%/°C]	Temp [°C]	DTG [wt%/°C]	Temp [°C]	DTG [wt%/°C]
[C]	[min]						
Untreated Biomass	–	295	0.10	368	0.67	489	0.05
	6	257	0.12	366	0.53	534	0.03
205	9	247	0.12	364	0.56	583	0.03
	12	241	0.10	366	0.52	593	0.03
	6	279	0.10	370	1.00	485	0.06
220	9	268	0.10	368	0.89	501	0.05
	12	272	0.13	361	0.96	494	0.05
	6	260	0.11	357	0.86	493	0.05
228	12	261	0.11	360	0.87	486	0.07

Pretreatment lowered initial decomposition temperature (T_{10}) that is attributed to modified structure and breakdown of hemicellulose from biomass as discussed later. However, almost no change in reaction intensity (wt%/°C) was observed at 10% of conversion ratio for pretreated materials. It indicates the increased reactivity of pretreated biomass since the equivalent reaction intensity was observed at lower temperature. No significant alteration in T_{50} was observed in pretreated residue although pretreatment decreased the corresponding reaction intensity (wt%/°C) when pretreatment temperature was 205 °C. When pretreatment temperature was further increased to 220 and 228 °C, reaction intensity was observed to increase significantly. Temperature at 90% of conversion ratio (T_{90}), which is an indication of overall conversion of pyrolysis process, showed that pretreatment at 205 °C made the biomass more resistance to thermal decomposition. However, further increase in pretreatment temperature to 220 °C and 228

°C showed the equivalent temperature (T_{90}) of pretreated biomass compared to untreated biomass.

4.3.2 Pyrolysis characteristics of untreated biomass

Biomass consists of three major components which are cellulose, hemicellulose, and lignin. It has been recognized that those components can be characterized by means of derivative thermogravimetry (DTG) [15,38]. In other terms, due to inherent difference in structure of those components, it is possible to qualitatively identify characteristics of those components from their intensity and location in DTG. In general, hemicellulose decomposition occurs within the range of 150 to 350°C, cellulose decomposes within the range of 350 to 500°C, and lignin decomposition ranges from 350°C to beyond 500°C [37].

Residual mass ratio and DTG of untreated biomass against temperature are shown in Fig.1. DTG distribution showed different peaks at different temperatures. The main peak appeared at around 384 °C that corresponds to decomposition of cellulose. Before cellulose peak (384°C), no definite peak was observed. Moreover cellulose peak was appeared unsymmetrical. According to Bridgeman [38], hemicellulose content in willow is around 14%. Therefore, it can be interpreted that low amount of hemicellulose in Salix makes hemicellulose decomposition to merge with cellulose decomposition, hence, attributed to the unsymmetrical shape at that region. Beyond 384°C, several broaden shoulders appeared at different temperatures. Those shoulders can be attributed to deformation of lignin components. This reflects that lignin of Salix decomposed in different steps during pyrolysis rather than having uniform decomposition over temperature. Upon observation, it should be pointed out that DTG of untreated Salix revealed different zone of decomposition for different biomass components. Therefore, it is possible to qualitatively justify changes in lignocellulos structure and its corresponding pyrolysis characteristics.
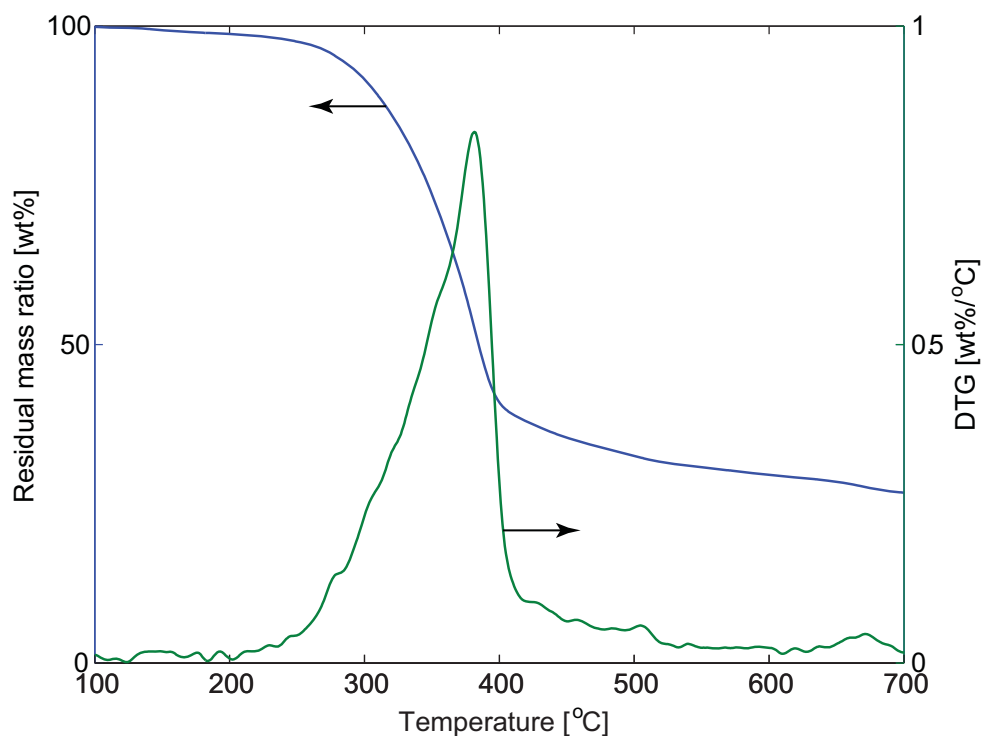
Fig. 1 Residual mass ratio and DTG of raw biomass as a function of reaction temperature

4.3.3 Change of biomass structure and pyrolysis characteristics by pretreatment

DTG distribution against temperature for pretreated biomass at 205 °C is shown in Fig. 2 with that of untreated biomass. Pretreatment times were 6, 9 and 12 minutes. In every occasion, the highest peak was identified at around 370°C. This peak stands for decomposition of cellulose. When pretreatment time was 6 minutes, a relatively broaden region with some small shoulders were observed before the cellulose peak (372 °C) in comparison with untreated biomass. That broadened region represents decomposition of transformed hemicelluloses. When pretreated residue produced at 205 °C and 9 minutes was tested, several peaks were observed before cellulose peak with a notable peak at 152 °C. Further increase of pretreatment time to 12 minutes showed only one peak at 153 °C.
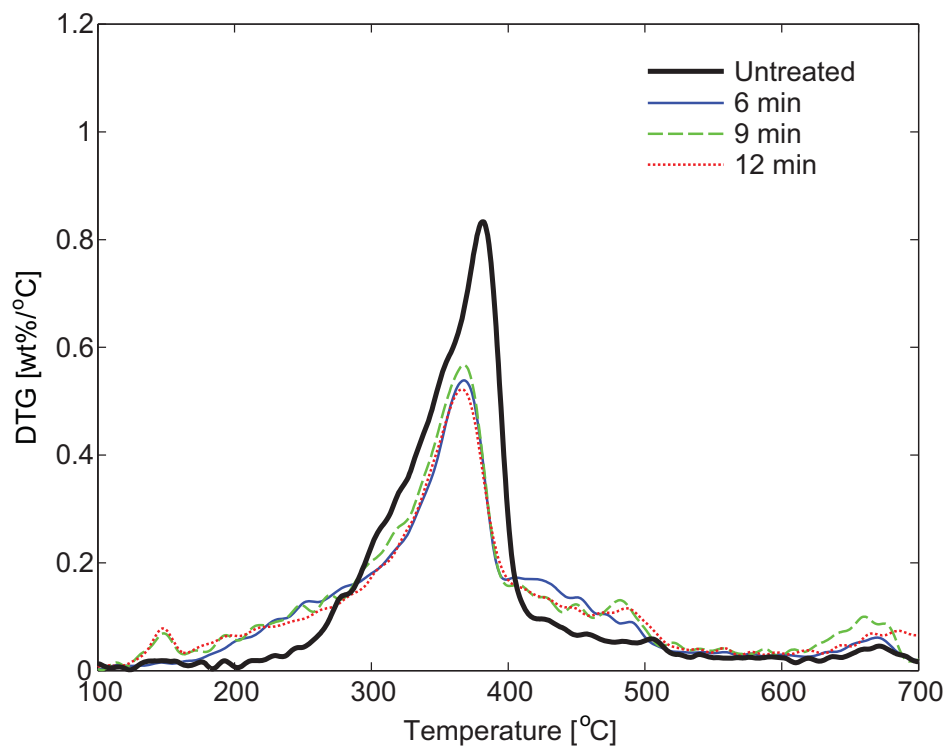
Fig. 2 Change of DTG distributions due to steam explosion (205 °C; 6, 9 and 12 min)
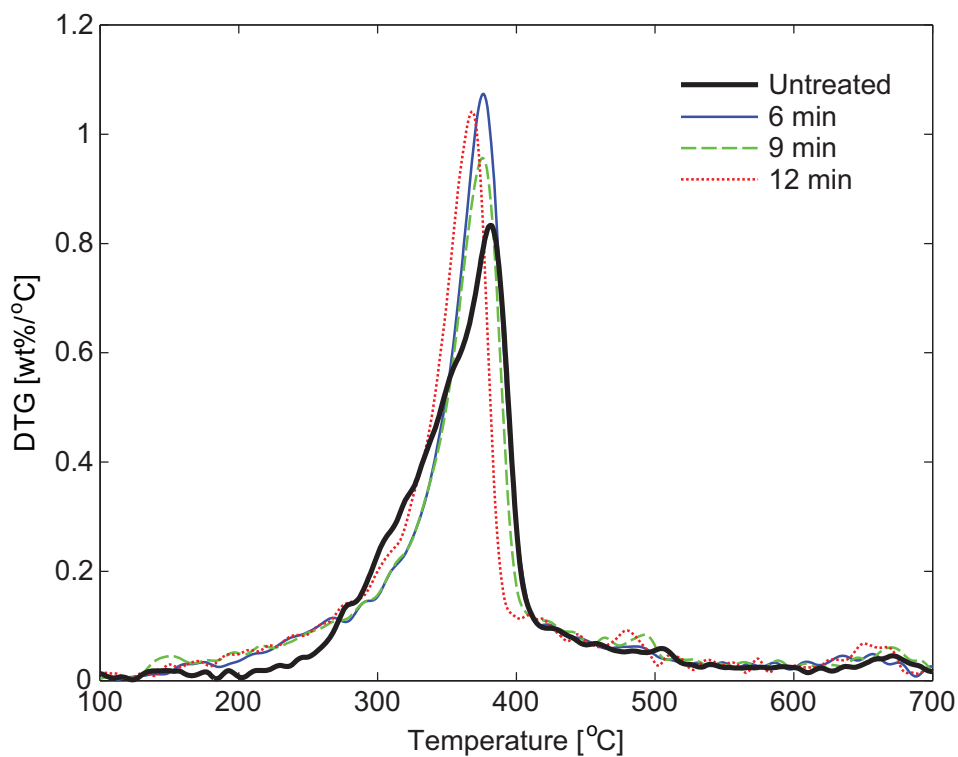

Fig. 3 Change of DTG distributions due to steam explosion at (220 °C; 6, 9 and 12 min)
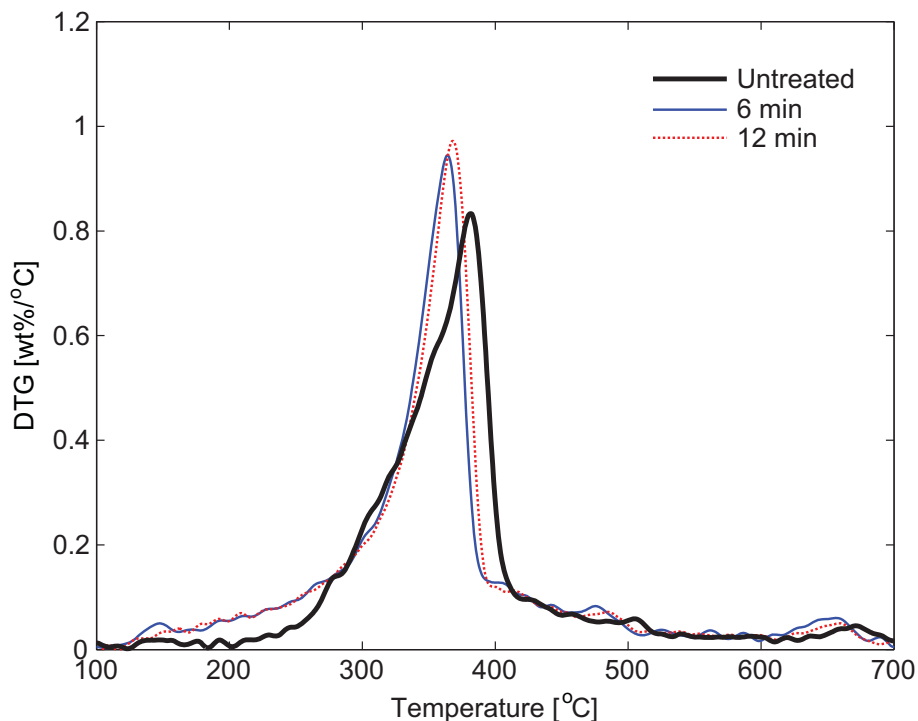
Fig. 4 Change of DTG distributions due to steam explosion at (228 °C; 6 and 12 min)

Figure 3 provides DTG distribution against temperature of pretreated residue when pretreatment temperature was 220°C for residence time 6, 9 and 12 minutes with that of untreated material. Similar to previous case (Fig. 2), a peak at around 150 °C was observed for pretreatment time 6 and 9 minutes before cellulose peak (370°C). However, further increment of pretreatment time to 12 minutes did not show any definite peak before cellulose peak. When pretreatment temperature was further increased to 228 °C (Fig. 4), peak at around 150 °C was observed for the case where pretreatment time was 6 minutes. However, no such peak in that region was observed when pretreatment time was 12 minutes.

The region before cellulose peak in every occasion showed overall higher intensity of decomposition comparing to untreated biomass. In addition, this region for pretreated biomass shifted to lower temperature zone than that of untreated biomass. In general, hardwood hemicellulose are mostly comprised of xylan (4-*O*-methylglucuronoxylans) [15]. This component goes through depolymerization reactions and reduces hemicellulose to smaller molecular weight components which in turn exhibit sensitivity to low temperature of pyrolysis. The observed peak at around 150 °C (Figs. 2, 3 and 4) can be attributed to the cross-linking reactions of liquefied D-xylose. D-xylose is the major monosaccharide of xylan and its melting point varies from 144 °C to 151 °C [39,40]. With the increment of pretreatment conditions, pretreatment temperature and time, hemicellulose can be hydrolyzed to monosaccharide. It can

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be thought that D-xylose molecules that had been distributed to the wood structure came into contact to other molecules after melting, and the cross-linking reactions occurred. Further increment of both pretreatment temperature and time (i.e. 220 °C and 12 minute) resulted in the disappearance of peak around 150 °C, which indicates the destruction of monomerized D-xylose to smaller molecules.

Cellulose maximum peak intensity varied incoherently with increase of pretreatment temperature. The peak intensities were found to be around 0.9 wt%/°C for the raw biomass, 0.5–0.56 wt%/°C for pretreated biomass at 205 °C, 0.95–1.03 wt%/°C for pretreated biomass at 220 °C, and 0.94–0.96 wt%/°C for pretreated biomass at 228°C. Previous studies showed that cellulose decomposition of biomass was related to alkali metal content and crystallinity of biomass [37, 41]. Higher alkali metal content tends to reduce cellulose decomposition temperature and rate during pyrolysis [41]. In our previous study, it was found that SE pretreatment reduced alkali metal content in biomass substantially [42]. Especially potassium (K) content was reduced with increase of pretreatment temperature. Therefore, no certain dependency of alkali metal on cellulose decomposition rate and temperature can be correlated.

To examine the effect of crystallinity on cellulose decomposition, X-ray diffraction (XRD) analysis was performed on three samples including untreated biomass. Figure 5 represents diffraction pattern with 2θ that varies from 10° to 30°. Two broad peak was observed at the 2θ values at around 15° and 22° for untreated biomass, which represents 101 and 002 lattice spacing in cellulose of wood [43]. Those peaks became narrow when biomass was pretreated at 205 °C for 12 minutes. XRD pattern of pretreated residue produced at 228 °C and 12 min exhibited similar narrow and intense peak at those positions. These observations suggest increase of crystallinity in pretreated biomass. Similar observation was made by Yamashiki and coworkers [44] for steam exploded residue. They explained that high temperature water penetrates to the paracrystalline and amorphous part of cellulose, and recrystallined the Paracrystalline by releasing free water molecule of wood cell. However, increased crytallinity does not show any dependency on cellulose decomposition. Ye and coworkers [45] observed increase in crystallinity in steam exploded biomass while they also observed reduction in mean hydrogen bond strength and degree of polymerization in steam pretreated biomass. Hence, nature of cellulose peak intensity in DTG might be also related to the strength of hydrogen bond and degree of polymerization. However, further detailed research is required to explain this nature of cellulose decomposition of pretreated biomass. Although both pretreatment parameters, temperature and time, played significant role in alteration of hemicelluloses, the effect of pretreatment temperature was more transparent on the thermal decomposition of cellulose under the examined conditions.
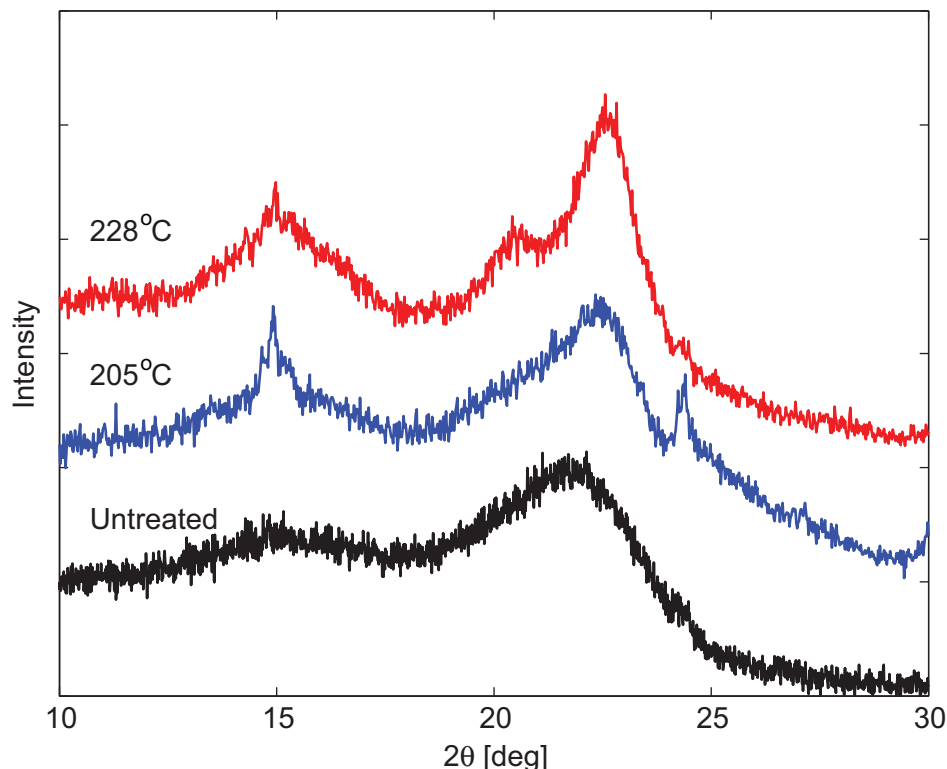
Fig. 5 XRD patterns of raw biomass and steam exploded biomass (205 °C and 228 °C; 12 min)

Significant alteration in the region beyond cellulose peak was also observed in pretreated residue. For pretreatment temperature of 205 °C and 6 minutes (Fig. 2), lignin decomposed gradually after cellulose peak. In every occasion, peak intensity was observed to be higher than untreated biomass. In addition, a definite shoulder was observed at around 670 °C for each pretreated samples. When pretreatment temperature was further increased (i.e. 220 °C and 228°C), in Figs. 3 and 4, the region beyond cellulose peak showed a slight shift towards lower temperature. This shift in peak can be suggested to the formation of thermolabile chemical bond due to increase of the severity of the process. However, intensity of those peaks reduced with the increase of pretreatment temperature from 205 °C to 220 °C and 228° C.Reduction in intensity of the lignin peak during increase of pretreatment temperature can be attributed to the increase of Klason lignin in the biomass due to condensation and repolymerization reaction between decomposition product of hemicellulose and lignin. According to Chau and Wayman [46], at drastic pretreatment conditions, some reactive components from hemicellulose such as furfural may react with lignin and increase the fraction of acid insoluble lignin in biomass. Ramons et.al [15] mentioned that at severe condition, lignin structure can be severely modified and it can increase the apparent yield of lignin. Hence, during thermochemical conversion, higher lignin content can lower the reactivity of biomass due to softening, melting and carbonization of lignin and partial blocking of the pores of the char [47].

Chapter 5

Devolatilization characteristics of steam exploded wood pellet

This chapter investigates the effect of pretreatment and reaction environment on devolatilization characteristics of pellet. This chapter is entirely based on **supplement III.** Devolatilization experiment was performed at different furnace temperature, 500 °C, 700 °C and 900 °C on the pellet produced from SE residue. Four pretreatment conditions were chosen. Pretreatment brought significant alteration in pretreated biomass devolatilization behaviour. Release of volatiles from depolymerized hemicellulose and lignin in wood along with subsequent development of flame affect the conversion of pellet to great extent. In addition, morphological structure of char was greatly influenced by those factors. In summary, severely pretreated biomass pellet took longer time to decompose in comparison with milder pretreated biomass.

5.1 Introduction

Devolatilization is one of the major conversion steps during combustion of solid fuels. Variation in the major components of biomass has significant impact on the reaction behaviour. Therefore, it is necessary to focus on the devolatilization characteristics of SE treated biomass. In previous chapter (Chapter 4), pyrolysis characteristics of steam explosion residue were investigated in nearly chemically controlled atmosphere. It was found that severe pretreatment condition produced more reactive biomass compared with mild pretreatment conditions [48]. In continuation of previous work, it has been extended to thermochemical behaviour of SE residue on the pellet. In this chapter, devolatilization characteristics of wood pellet produced from SE residue is focused.

The aim is to observe the effect of SE conditions (i.e. Temperature and Time) on the reactivity of woody biomass pellet. Conversion behaviour and morphological structure of char were examined to address the effect of pretreatment on change of devolatilization characteristics of pellet. Salix chips were used as samples for SE pretreatment. Wood Pellets were produced from SE residue, thereafter; the pellet was subjected to high temperature air to examine its devolatilization characteristics under different furnace temperatures.

5.2 Experimental

5.2.1 Raw material and Equipment

Four treated biomass was chosen to investigate devolatilization of pellet. Table 1 represents the pretreatment conditions. Two process parameters were varied; temperature and time. Two pretreatment temperatures were chosen: 205, and 228 °C. Pretreatment time was chosen as 6 min and 12 min. The steam used was in saturated condition. The pretreatment cases have been separated into two categories, milder and severe pretreatment.

Table 1: Pretreatment conditions used for experiment

Cases		Pretreatment conditions	
		Temperature [°C]	Time [min]
Milder pretreatment	1	205	6
	2	205	12
Severe pretreatment	3	228	6
	4	228	12

 Prior to pelletizing, the pretreated residues were screened through 0.5, 1 and 1.4 mm sieve. A 12 mm diameter of cylindrical mold was used to make pellet. Pelletizing was performed in a piston press at room temperature. The pellet density varied from 1220-1240 Kg/m^3. To determine the devolatilization characteristics of pellet, a laboratory scale furnace was used. Fig.1 presents the schematic diagram of thermochemical treatment facility. Detailed description of the facility can be found elsewhere [49]. The furnace was heated by combustion of natural gas up to certain temperature. Thereafter, the furnace was purged with air to avoid presence of other gases. The sample was inserted from the top of the reactor and suspended on a precision scale to measure the mass loss. The furnace has an observation window and a video camera was used to record the devolatilization behaviour.
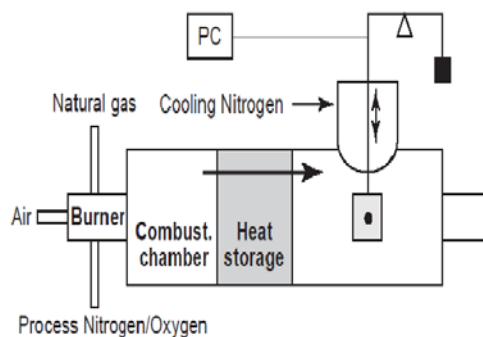
Fig. 1: Schematic presentation of Laboratory furnace used for the experiments

Devolatilization experiments were performed under air environment at 900 °C, 700 °C and 500 °C for milder pretreated biomass pellet (Case 1 and 2). For severe pretreated pellet (i.e. Case 3 and 4), furnace temperature was 900 °C and 700 °C. The mass loss of the pellet was recorded by data acquisition system from initial drying to end of flaming pyrolysis. After pyrolysis, char was cooled by nitrogen in a separate chamber and char dimensions were measured. Video recording from the camera was used to track the ignition and end of flaming pyrolysis.

Morphological structure of char for some samples was analysed by Scanning Electron Microscopy (SEM) equipped with Energy Dissipation X-ray Spectroscopy (EDS). EDS was used to analyse the formed mineral content on the char structure.

5.2.2 Definition of parameters

 The devolatilization process was analysed by using the following definitions

  a. Devolatilization time was considered from the moment when the pellet was inserted inside the chamber till the flame around the pellet disappeared. Therefore, it contains drying, flameless pyrolysis and flaming pyrolysis.
  b. In some occasions, char oxidation was observed before volatiles were ignited. It is defined as the glowing of the char. Glowing time is defined from the moment the pellet was inserted inside the chamber until the char surface starts glowing.
  c. Ignition time is defined from the moment the pellet was inserted inside the furnace until volatiles were ignited.

5.3 Results and Discussions

5.3.1 Effect of SE condition on Devolatilization Characteristics

To have comprehensive view on devolatilization characteristics of SE pellet, different phenomena, such as glowing time, ignition time, and devolatilization time are listed in Table 2 at different furnace temperature. No significant difference on ignition time and total pyrolysis time was observed in pretreated biomass pellet samples when the furnace temperature was 900 °C. This is attributed to the high heat transfer rate caused due to high furnace and gas temperature which eventually enhanced decomposition rate. When furnace temperature was reduced to 700 °C, delay in ignition time and increase in pyrolysis time was observed. Additionally, glowing was observed in severely pretreated residue (i.e. Case 3 and 4). Further decrease in furnace temperature resulted in both delay in ignition time and devolatilization time.

Table 2: Glowing time, Ignition time, and Devolatilization time of SE pellet under different furnace temperature

Furnace Temp (°C)	900			700			500		
Pretreatment cases	Glowing	Ignition	Devolatilization	Glowing	Ignition	Devolatilization	Glowing	Ignition	Devolatilization
[-]	[sec]	[sec]	[sec]	[sec]	[sec]	[sec]	[sec]	[sec]	[sec]
1	N.a	2	102	N.a	11	115	Na	91	190
2	N.a	1	102	N.a	16	129	62	103	153
3	N.a	2	97	7	12	129	N.a	N.a	N.a
4	N.a	3	119	8	13	133	N.a	N.a	N.a

5.3.2 Effect of SE condition on mass loss rate characteristics

5.3.2.1 Milder pretreated biomass

Derivative mass loss distribution against time for pellet from case 1 and 2 is shown in Fig. 2 for different furnace temperature 900 °C, 700 °C, and 500 °C, respectively. Ignition of pellet took place immediately after insertion inside the furnace at temperature of 900 °C (See table 2). Immediate ignition of volatiles is attributed to the rapid release of volatiles due to high atmospheric and gas temperature (i.e. 900 °C). Later on, pellet decomposed rapidly due to high heat transfer through the pellet caused by the developed flame. In addition, decomposition rate from case 2 became higher after around 24 sec in comparison with case 1.
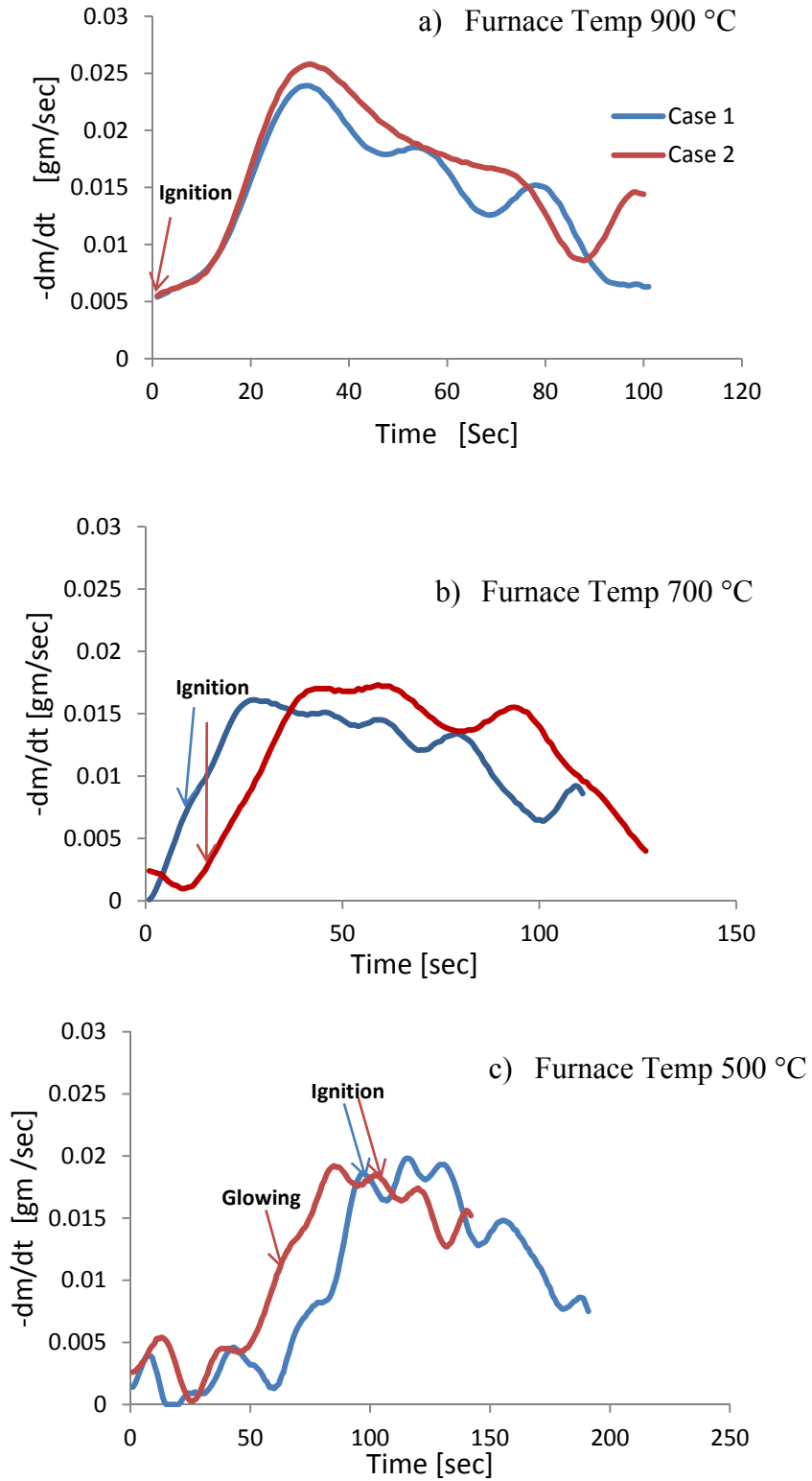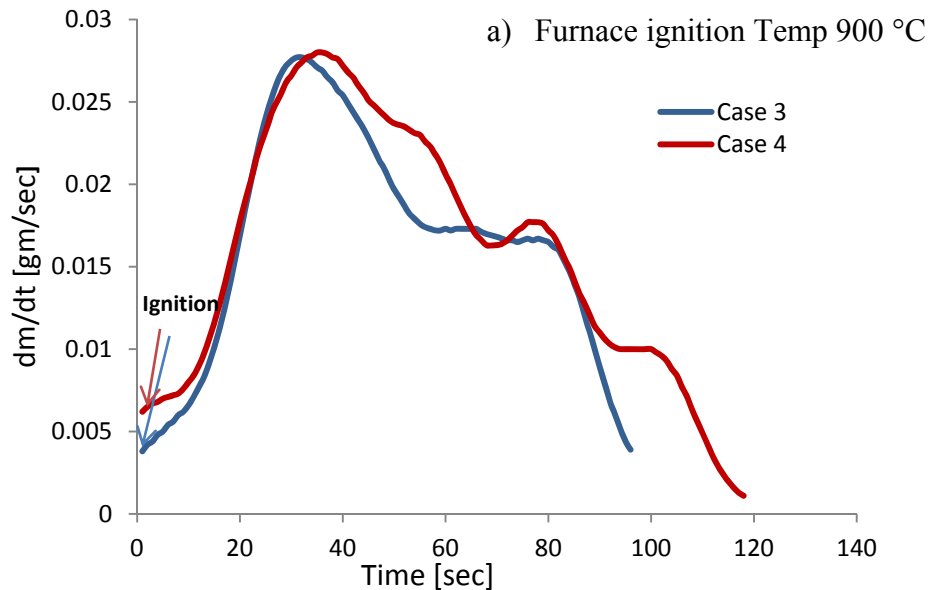
Fig. 2: Decomposition rate for milder pretreated biomass pellet at furnace temperature of 900 °C, 700 °C and 500 °C, respectively

When pretreated biomass pellets were tested under furnace temperature of 700 °C (Fig. 2b), difference in ignition time was observed. Although decomposition rate of pellet from case 2 was higher initially, pellet produced from case 1 ignited immediately whereas delay in ignition was observed for pellet from case 2. Late development of ignition delayed the conversion of pellet form case 2 in comparison with case 1. Although the decomposition of pellet from case 2 was delayed, the mass loss rate was higher after 38 sec of conversion in comparison with case 1. Further reduction in furnace temperature to 500 °C brought significant difference in devolatilization characteristics of pretreated biomass. Char oxidation (defined by glowing) was observed in pellet from case 2 prior to the development of flame from volatiles. In this occasion, decomposition of pellet was governed not only by conduction of heat from atmosphere but also the heat produced by oxidation of char in the pellet. This effect enhanced conversion rate which promoted faster decomposition of wood pellet.

In every occasion Ignition of volatiles took place earlier in case 1 in comparison with case 2. In our previous study [48], it was found that steam explosion pretreatment significantly alter pyrolysis characteristics of biomass through mainly depolymerization of hemicellulose, and lignin. Increase of pretreatment severity (i.e. from 6 min to 12 min) further reduced hemicellulose to monosaccharaides which are sensitive to lower temperature. Additionally, hemicellulose content in biomass was also reduced with increase of pretreatment severity. When pellet was introduced into hot environment, initial decomposition of pellet is attributed mainly to the decomposition of smaller molecules from hemicellulose. Since SE pretreatment depolymerized the hemicellulose to smaller molecules (i.e. case 1) then to monosaccharaides (case 2), initial decomposition rate of case 2 was higher than case 1 at furnace temperature of 700 °C and 500 °C. Although initial decomposition rate was higher for case 2, ignition took place later than case 1. This can be attributed to the absence of right air-fuel ratio since hemicellulose amount was also reduced with increase of pretreatment severity. When flame was developed around the pellet, rapid decomposition rate was observed in every occasion. Moreover, pellet from case 2 decomposed at higher rate in later part of the conversion at furnace temperature of 900 °C and 700 °C. It is due to presence of lignin which decomposed at higher temperature [10]. Therefore, major decomposition took place when the pellet temperature was increased due to developed flame.

5.3.2.2 Severely pretreated biomass

When the furnace temperature was 900 °C, both severely pretreated biomass ignited immediately (see figure 3a). Further reduction of furnace temperature to 700 °C showed different devolatilization behaviour in comparison with milder pretreated biomass. Initially both hydrolysis pellet showed heterogynous char oxidation prior to ignition of volatiles. In addition, both char oxidation and ignition took place almost at the same time. Unlike milder pretreated biomass (see section 3.2.1), severely pretreated biomass showed both earlier development of char oxidation and ignition. In our previous study, it was observed that the pyrolysis of those both hydrolysis residues showed almost identical behaviour. In addition, hemicellulose of those cases was severely depolymerized from monomerized d-xylose to even smaller molecules, hence reduce the amount of hemicellulose in biomass. This revealed, while decomposing, most of the decomposition came from decomposition of lignin which probably is difficult to ignite due to absence of right air-fuel ratio. This effect enhanced the diffusion of oxygen into char surface and promoted char oxidation. This early development of char oxidation increased the average temperature of the pellet which eventually helped to develop the flame. Likewise milder pretreated biomass, case 4 decomposition rate increased in later part of the conversion.
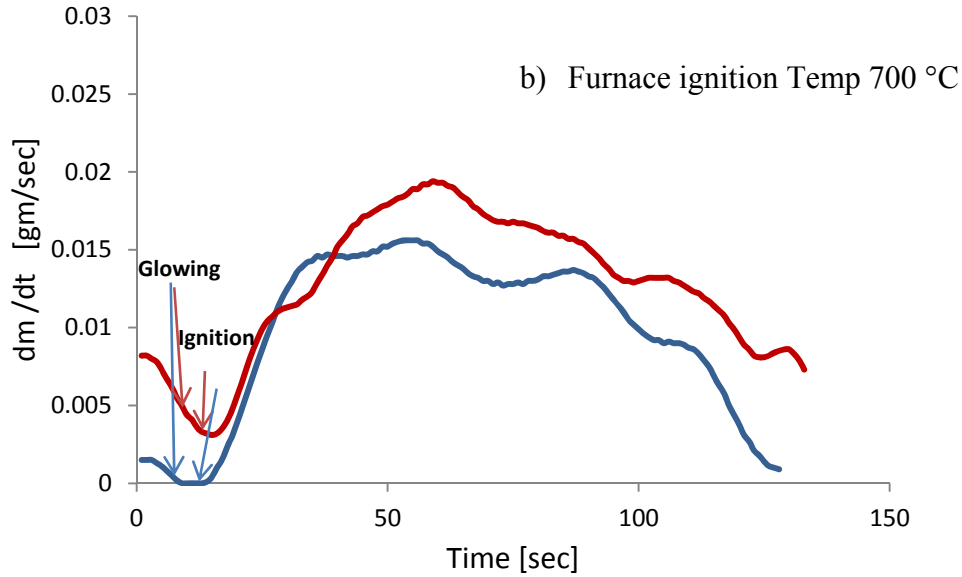

a) Furnace ignition Temp 900 °C

Fig. 3: Decomposition rate for severely pretreated biomass pellet at furnace temperature of 900 °C, and 700 °C, respectively

5.3.3 Char Structural changes

Effect of pretreatment on produced char dimension can be found in Table 3. Shrinkage along the radial direction was observed in all experimental cases. In addition, Shrinkage along longitudinal direction was observed in pretreated pellet for case 4 at furnace temperature of 900 °C and 700 °C and also for those cases when furnace temperature was 500 °C. However, expansion in longitudinal direction was observed for pretreated case 1, 2 and 3 for furnace temperature of 900 °C and 700 °C.

Table 3: Longitudinal and radial dimensional change of SE pellet

Furnace Temp (°C)	900		700		500	
	$(l.l_0)/l_0$	$(d-d_0)/d_0$	$(l-l_0)/l_0$	$(d-d_0)/d_0$	$(l-l_0)/l_0$	$(d-d_0)/d_0$
Pretreatment case	[%]	[%]	[%]	[%]	[%]	[%]
1	13,69	-12,5	16,1	-14,58	-1,48	-12,5
2	19,89	-8,33	13,4	-13,33	-4,54	-8,33
3	0,5	-12,5	8,62	-14,58	Na	Na
4	-4,54	-16,67	-0,27	-13,33	Na	Na

l_0- Initial Length of Pellet d_0-Initial diameter of pellet

l- Final length of pellet   d-Final diameter of pellet

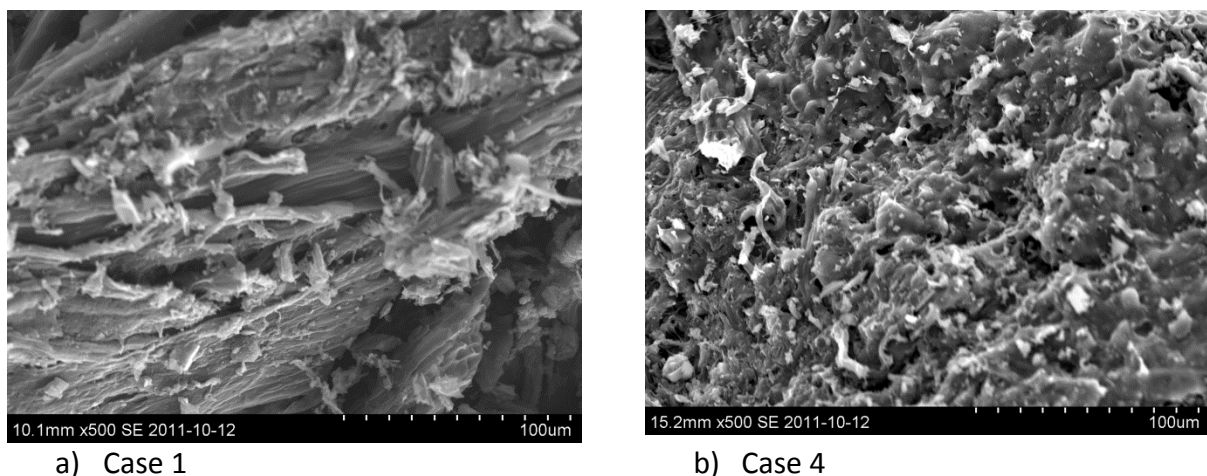a) Case 1   b) Case 4

Fig. 4: SEM of Char for pretreated case 1 and 4 at 900 °C of furnace temperature

To examine the reason of expansion in pretreated biomass pellet, Scanning Electron microscopy (SEM) was performed on the char from case 1 and 4 at furnace temperature of 900 °C. Fig. 4 shows SEM of char produced from pretreated residue. Char from milder pretreated (case 1) showed more distorted structure in comparison with severely pretreated biomass (case 4). More distorted structure of char in milder pretreated case can be attributed not only to the heating rate but also composition of wood. Presence of depolymerized hemicellulose in milder pretreated biomass pyrolyzed rapidly during heating up of the particle and increased the pressure inside the pellet followed by rapid release through the fibres, hence, caused expansion of pellet. On the other hand, shrinkage can be attributed to slow release of volatiles followed by development of small pores in severely pretreated biomass.

5.3.4 Ash analysis

The ash formed on the char surface was analysed by SEM-EDS. It was found that the main ash component in molten form is Calcium for case 1, and 2 at 900 °C. However, case 1 at 500 C showed significant amount of Mg, Al, Si, K, and Fe which indicates higher ash sintering tendency of milder hydrolysis residue when operating temperature is low.

Chapter 6

Process simulation of torrefaction

This chapter is intended to address the process aspects of torrefaction. In recent years, different claims have been made on the efficiency of torrefacion process. However, no definite picture can be found from open literature. Process analysis of torrefaction process was performed by using commercial software Aspen Plus ™. The efficiency of the process varies from 80-90 %. Decisive factors for process efficiency are both choice of process conditions and type of biomass. Therefore, choice of appropriate process conditions along with type of biomass is important for the whole process.

6.1 Introduction

Torrefaction of biomass was first reported to be in 1930's [50]. Later on, during 80's, torrefaction of biomass was investigated in demonstration scale which followed to dismantling of the plant during 90's due to lack of complete comprehension of the process. During the beginning of this century, torrefaction again draw attention in research. A wealth of research has been performed on torrefaction mainly by Berman et.al [51-54]. They have demonstrated that torrefaction can bring superior improvement both in the properties and logistics of fuel. Torrefaction process is now being emerging from research and development stage to commercial scale.

During torrefaction process different types of product evolves which can be lumped into three groups, solid, condensable gases, non-condensable gases. Those product yields are highly influenced by the process parameters such as temperature and time [52]. Although a reasonable amount of publications is available on torrefaction, few of them provided the whole spectrum of product yield. For Instance, Prins et al. has [18] reported a wide spectrum of product yields from the torrefaction process.

Different promising claims have been made on process efficiency of torrefaction. Some studies, mainly by commercial sectors, claims that the process efficiency is around 95% whereas according to Ciolkosz D [17], the real process efficiency is around 80% or less. Ambiguity in available information may lead to misinterpretation of this technology. Therefore, investigation of process performance has outmost importance when realizing such technology in commercial scale. ASPEN PLUS ™ [55] is commercial software which provides opportunity to perform

thermodynamic analysis of processes. This package includes necessary thermodynamic properties of most of the chemical substances.

The objective is to perform performance analysis of a typical torrefaction process. It includes determination of critical process parameters and their influence on the overall process performance.

6.2 Methodology

6.2.1 Process Concept and model development

The process concept is shown in Figure 1. Initially, wet-biomass was dried in a dryer with flue gas to desired moisture content to 10% from 20 %. The drying temperature was considered as 110°C to provide sufficient energy for drying and avoiding saturation of the gases and volatilization of biomass. Afterwards, dried biomass was subjected to torrefaction at certain process condition by using majority of torrefaction gas. The reason of using torrefied gas is to ensure inert atmosphere for torrefaction process. Torrefaction gas was used as main energy carrier for the process. If the process required additional energy, due to higher moisture content, part of the torrefied biomass was used as auxiliary fuel.
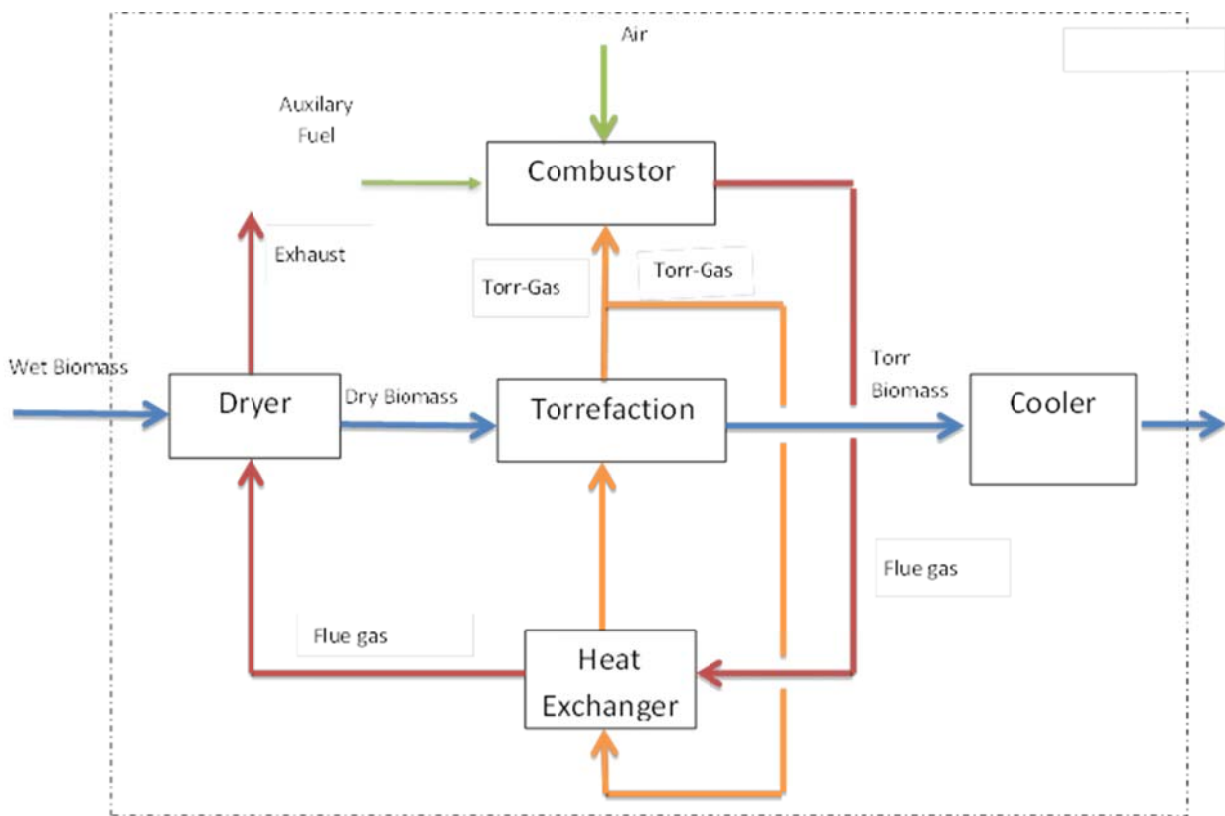
Fig. 1 Process Flow Diagram for torrefaction process

Three types of wood was selected, hardwood, softwood and agricultural residue. The properties of biomass are listed in Table 1. The initial moisture content of the biomass was considered as 20% for each type of biomass.

Table 1 Biomass properties

	Ash	C	H	N	O	O/C	HHV(MJ/Kg)
Willow	1,6	47,2	6,1	0,34	44,8	0,71	19
Larch	0,1	48,8	6,1	0,1	44,9	0,69	19,5
Straw	7,1	44,3	5,8	0,4	42,4	0,72	17,4

Modeling was performed with ASPEN Plus ™ [55]. Drying of the biomass was performed in a stoichiometric reactor without considered any real chemical reaction. Detailed procedure of drying can be found in Aspen plus tutorial [55]. Water evaporation of was considered as chemical reaction as an input for the model. Since no reliable model for torrefaction of biomass is available, the torrefaction reactor was modeled based on experiment results from Prins and

Ferro [18, 56]. Combustion of gases and solid was performed by using Gibbs energy minimization criteria.

6.2.2 Used Parameter

To describe the result comprehensively, a parameter was used, namely, Energy retained.

$$Energy\ Retained, RE = \frac{mass\ of\ torrefied\ product \times HHV\ in\ product}{mass\ of\ feed\ biomass(db) \times HHV\ in\ feed\ biomass} \tag{1}$$

6.3 Results and Discussions

The effect of the type of biomass on total recovery of product is quite evident. Figure 2a shows total recovery of solid after satisfying all process requirements (i.e. using part of the torrefied biomass for process heat). Softwood (Larch) seems to retain most of the solid in comparison with agricultural residue and hardwood (Willow). Unambiguous way of representing the product of this process is in terms of energy retained in the solid product. In accordance with mass recovery, energy retained (RE) shows similar behavior for all of those wood species (see Figure 2b). For instance, softwood (Larch) can retain most of the energy from the biomass. On the other hand, RE of agricultural residue (Straw) is relatively low due to its fibrous structure. On the other hand, for hardwood, two possible reasons can explain the lower value of RE. Hemicellulose structure of the hardwood is more sensitive to thermal decomposition and also higher in quantity in comparison with softwood (i.e. Larch).Due to higher decomposition of the hemicellulose; the RE of the product reduces. Additionally, torrefaction of hardwood produces more reaction water which reduces adiabatic flame temperature of the produced gas (torr-gas) during combustion. This results in higher consumption of auxiliary fuel to deliver process heat. Since, in this process, auxiliary fuel used was part of the torrefied biomass, it evidently impacted on the product yield. Upon observation, Softwood seems to produce more useful product in comparison with hardwood and agricultural residue.
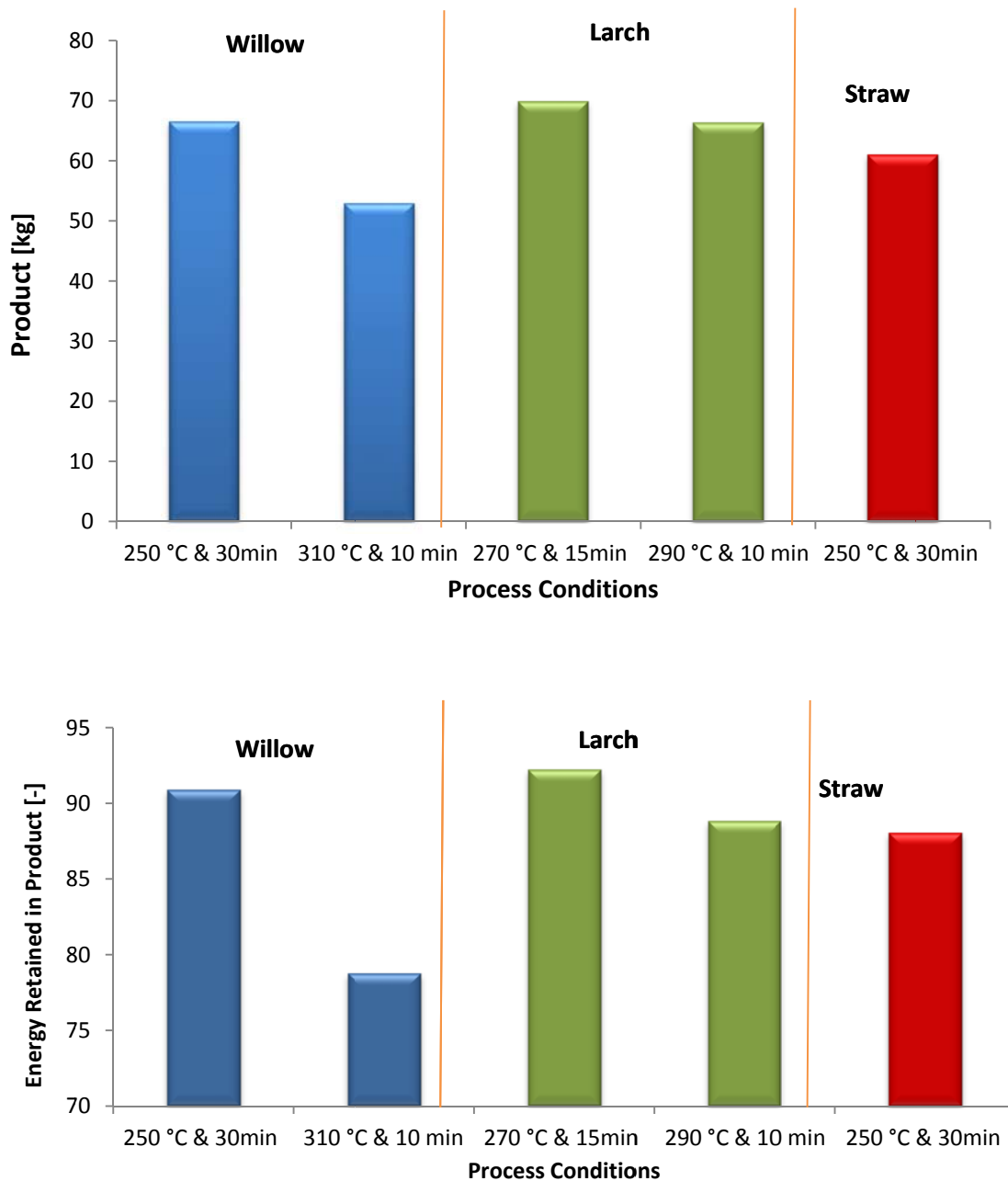
Fig. 2 (a) Total recovered solid (torrefied biomass) after the process (b) Energy Retained in Product

Evidently, torrefaction temperature has significant effect on the RE (Eq. 1) of the biomass (See Figure 2). For instance, When Willow was treated at 250 °C; the RE was around 90%. Further increase of temperature to 310 °C reduced the RE to 78%. Similar pattern can be also observed for softwood. The main reason behind that is the temperature above 270 °C, cellulose starts decomposing along with hemicellulose. As a result, biomass starts realizing most of its energy as volatile. Therefore, Choice of operating condition is decisive in terms of RE .

Effect of process conditions becomes evident by observing the process efficiency (see Figure 3). Severe process condition leads to lower process efficiency both for soft and hardwood. Reduction in process efficiency was because of operation of the process above auto-thermal.
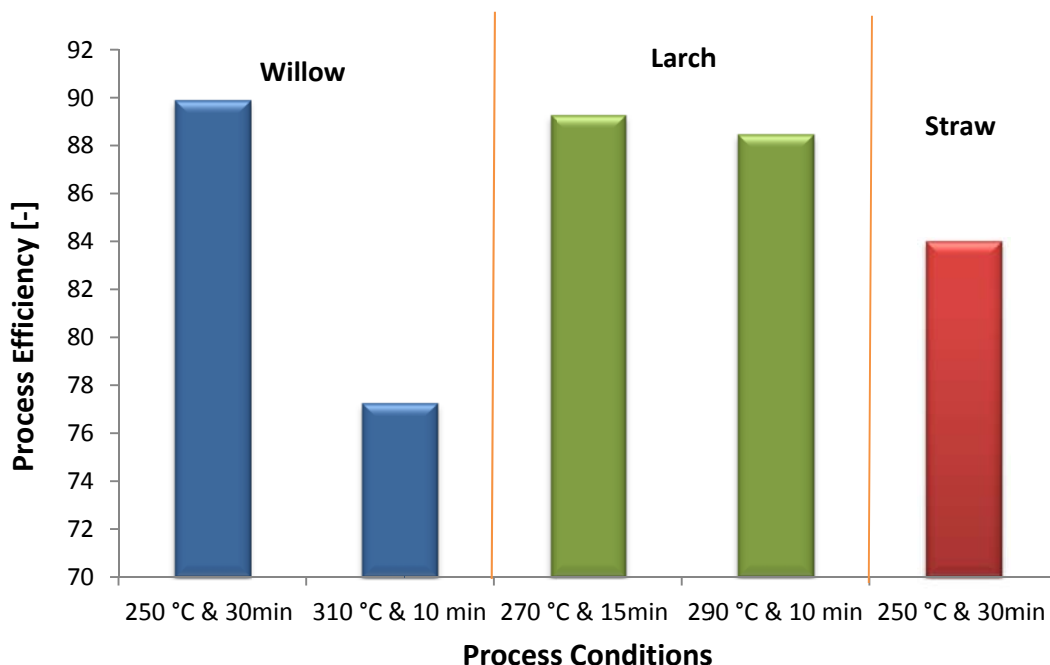

Fig. 3 Overall Process efficiency

In line with previous observations, types of wood have also significant effect on process efficiency. Larch seems to provide more efficient process even at severe condition. In contrary, Willow provides lower efficiency at severe condition. The main reason would be the production of higher reaction water for Willow(7 – 12 %w/w) during torrefaction in comparison with Larch (4-6 % w/w) which leads to reduction in adiabatic flame of the torr-gas . On the other hand, when straw was torrefied at almost similar condition to other biomass, process efficiency was reduced to 84%. The main reason is that the production of excessive amount of volatiles. The heat content of these volatiles cannot be entirely used by the process.

Chapter 7

Concluding remarks

The final chapter addresses final conclusions of this thesis. Additionally, further recommendation is also addressed for future research.

7.1 Concluding discussion

7.1.1 Pretreated biomass thermochemical aspects

Steam explosion pretreatment is striking in context of alteration in elementary composition of fuel. Greater degree of carbonization and removal oxygenated compounds leads to increase in heat content of the fuel. Total amount of ash was also reduced in pretreated residue. Although steam pretreatment shows promise in terms of reducing alkali and heavy metal components of biomass, degradation in ash fusibility was observed in steam treated residue. Pellet produced from steam treated residue showed increase in physical properties of pellet such as higher density, impact resistance, and abrasive resistance

When pyrolysis on SE residue was performed, significant alteration was observed in the structure and pyrolysis characteristics of biomass. At pretreatment temperature of 205 °C, biomass became more resistance to thermal decomposition. While hemicellulose decomposition rate was increased, cellulose decomposition peak intensity was reduced significantly in pretreated residue in comparison with untreated biomass. Likewise, pretreatment also enhanced thermal stability of lignin at this pretreatment condition. Increment in pretreatment temperature to 220 and 228 °C resulted in the increase of cellulose decomposition peak intensity. On the other hand, lignin decomposition rate reduced at severe conditions due to apparent increase of lignin. However, lignin content of pretreated biomass under severe conditions decomposed earlier than that of pretreated biomass under mild conditions. Hence, severe pretreatment condition seems to produce more reactive biomass compared with mild pretreatment conditions. In addition, increase in cellulose crytallinity was observed in pretreated residue. However, no clear dependency of cellulose peak intensity on either crystallinity or alkali metal of biomass was observed.

When devolatilization experiment was conducted on pretreated biomass pellet, the effect of fuel was observed on its conversion behaviour. When furnace temperature was 700 °C and 500 °C, Conversion characteristics of pretreated biomass pellet are largely affected by the initial release of volatiles and subsequent development of flame around the pellet. Milder pretreated biomass decomposed earlier in comparison with severely pretreated biomass due to decomposition of depolymerized hemicellulose and thermo-liable lignin. On the other hand, conversion of severely pretreated biomass (i.e. case 3 and 4) takes longer time due to presence of lignin which is

sensitive to higher temperature. However,   at higher furnace temperature (900 °C), the effect of pretreatment on pellet from SE residue was not evident on its devolatilization behaviour. Analyzing morphology of char revealed that milder pretreated biomass was extremely distorted due to de-compressive release of volatiles which leads to expansion in pellet length. In addition, ash analysis on the surface of the char at 500 °C revealed that hydrolysis residue probably has higher ash sintering tendency.

7.1.2 Process aspects of Torrefaction

Biomass type has significant effect on both product yield and process efficiency. Softwood (Larch) tends to provide higher process efficiency in comparison with hardwood (Larch) and agricultural residue (Straw). On the other hand, choice of process condition has great importance when considering process efficiency. Extreme process condition may lead to excessive mass loss, hence, reduction in process efficiency. Therefore, it is advisable to operate process under less severe condition, hence, below auto-thermal point to maximize process efficiency. Although process efficiency was observed to be around 80-90%, it can be significantly improved by recovering heat from cooling water of the solid which can be used as preheated water for district heating system. Therefore, desirable process performance can be achieved by choice of biomass, process condition and effective way of using low quality heat of the system.

7.2 Main Conclusions

Steam explosion pretreatment improves fuel quality by enhancing its heat content, and reducing ash, alkali and heavy metals content, in biomass. However, ash fusibility was observed to reduce in SE residue. When pellet was produced from SE residue, it showed significant improvement in its quality. Pellet properties, such as density, impact and abrasive resistance were improved.

When pyrolysis on SE residues was performed, it was observed that due to change in fundamental structure of biomass during SE, pyrolysis characteristics were also altered. Contribution from depolymerized components (hemicellulose, cellulose and lignin) of biomass could be observed explicitly during pyrolysis. When devolatlization experiment was performed on pellet produced from SE residue, contribution of those altered components could be observed. In summary, pretreated biomass fuel characteristics is significantly different in comparison with untreated biomass.

On the other hand, Process efficiency of torrefaction process is governed by choice of appropriate process condition depending on the type of biomass. It is advisable to operate process under less severe condition, hence, below auto-thermal point to maximize process efficiency.

7.3 Recommendations for future work

This thesis addresses some features of pretreated biomass. However, main research should be focused on the detailed investigation of thermochemical decomposition behavior of SE residue considering different particle size. The purpose would be to examine the effect of mass and heat transfer on pretreated biomass and develop a fundamental concept. Of outmost interest would be to investigate performance of pretreated biomass in different thermochemical processes such as gasification and pyrolysis. Since during pretreatment oxygen is lost, it might also be interesting to investigate the fate of pretreated biomass for Bio-oil production. Perhaps, it can reduce the water content in the oil.

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