Co-pyrolysis of sugarcane bagasse and scrap tire in fixed-bed reactor

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I certify that this research work titled "*Co-pyrolysis of sugarcane bagasse and scrap tire in fixed-bed reactor*" is my own work. The work has not been presented elsewhere for assessment. The material that has been used from other sources it has been properly acknowledged / referred.

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Abstract

The study investigated usability potential of scrap tire and sugarcane bagasse as co-pyrolysis feedstock with a focus on liquid yield. Two raw materials were fed to fixed-bed reactor in various mixing ratios. The experiments were carried out at 500 °C with heating rate of 20 °C/min and Nitrogen flow rate of 50mL/min was used as carrier gas. Sugarcane bagasse/scrap tire 1:3 produced highest liquid yield which was 49.7 wt.% against 42.1 wt.% of pure sugarcane bagasse. Oil from sugarcane bagasse, scrap tire and their blend 1:3 was then characterized for physical and chemical properties using different chromatographic and spectroscopic analytical techniques. Significant synergistic effects were indicated by the quality and quantity of the co-pyrolysis liquid yield. The optimum feedstock mix produced oil with calorific value of 41 MJ/Kg with significantly lesser viscosity as compared to pure sugarcane bagasse pyrolysis oil. Co-pyrolysis oil showed high potential to be used as feedstock for fuel production after required processing.

Key Words: Co-pyrolysis, Sugarcane bagasse, Scrap tire, Pyrolysis oil

CHAPTER 1

INTRODUCTION

1.1 Background

Due to the rapid increase in global population and technological development, energy demand is increasing rapidly and proven reserves of conventional energy resources are depleting (Isahak et al., 2012). It is reported that the fossil fuel reserves will be depleted within the next 100 years with a 60% increase in energy demand by 2040. The enormous amount of research has been carried out to explore more sustainable resources of energy (Lu et al., 2009). Considering such pursuits in last 30 years, biomass individually accounts 56% of the total research studies focused on renewable energy sources followed by 26, 11, 5 and 2% for solar, wind, geothermal and hydropower (Dewangan et al., 2016).

Keeping the fossil fuel combustion technology developed throughout the history in view, biomass is the only renewable energy which has potential to supplement decreasing crude oil and coal reserves without increasing net CO_2 concentrations in the atmosphere as CO_2 released during its combustion is same as extracted from the atmosphere during its growth (Ateş, 2011). Biomass is rich in hemicellulose, cellulose and lignin components having high contents of energy (Tsai et al., 2006). By using different thermal and biological techniques it can be converted into liquid, solid and gaseous fuels (Dewangan et al., 2016).

Sugarcane is a major agricultural crop found in subtropical and tropical regions (Garcıa-Perez et al., 2001). It is estimated that 280 kg of SCB is produced out of each ton of sugarcane processed (Cardona et al., 2010). Unlike growing fuel specific crops, utilizing sugarcane bagasse (SCB) as energy resource has no impact on food production and food price (Carrier et al., 2011). At present SCB is mostly used in sugar mills for electricity production by steam generation in boilers having very low efficiency (up to 26%) (Garcìa-Pèrez et al., 2002). Small amounts of SCB are also burnt to provide heat required for sugar processing which may result in significant health problems in surrounding areas because of airborne ash generation (Rabelo et al., 2011) . One cleaner way to extract energy out of SCB is to convert it into renewable fuels such as bio oil, char and gas which can considerably raise the profit of sugarcane crop. These liquid, solid and gaseous fuels can also be transported to long distance users (Asadullah et al., 2007).

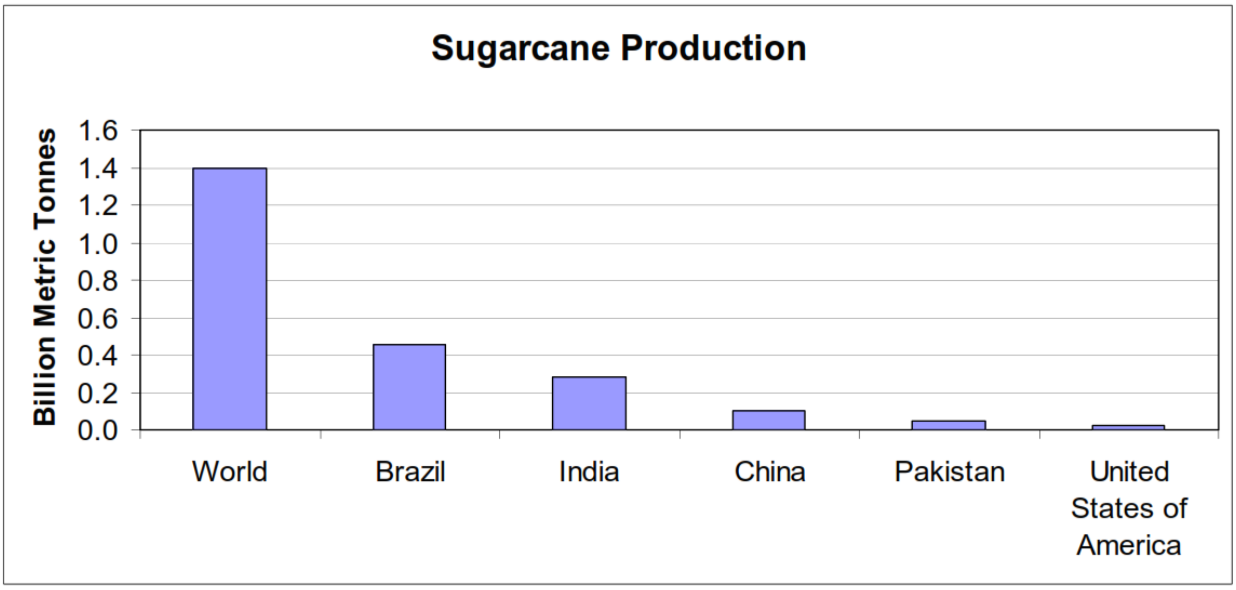

Figure 1: Sugarcane production in year 2016 for entire world and countries which are sugarcane production leaders is represented (Cardona et al., 2010).

On the other hand, scrap tire (ST) is a fossil based waste. About 1.5 billion tires are produced each year around the world (Uçar et al., 2014).Unfortunately ST is also used for heat generation by direct combustion, posing bigger impact on air quality with small energy gain (Kar, 2011). Both ST and SCB have shown great potential to be used for the production of different types of fuels (liquid, solid and gas) using appropriate technique such as pyrolysis process (Samolada et al., 1998).

Pyrolysis is an old, common and viable thermochemical conversion process which has long been explored as mean of transforming biomass into more useful fuel products (Garcia-Perez et al., 2007). The quantity and quality of the pyrolysis yield is affected by various process parameters (e.g. heating rate, temperature, residence time, pressure) (Guo et al., 2017), reactor type (Isahak et al., 2012), feedstock type and characteristics (size, structure and shape) (Akhtar et al., 2012). For biomass pyrolysis in general, temperature range of 400-550 °C is ideal to enhance liquid yield production, whereas pyrolysis temperature greater than 550 °C and less than 400 °C enhance the gas and solid yield quantity respectively (A. Bridgwater, 1999). Even though pyrolysis process itself does not contribute towards emission of harmful pollutants, the properties of pyrolysis products of biomass, however, vary with the previously mentioned factors and have been generally reported to be poorer as compared to fossil fuels (Guillain et al., 2009). Low heating value, low combustion efficiency and high water content of biomass pyrolysis yields make it inappropriate to be used as fuel without prior significant processing (A. Bridgwater et al., 1999) . Similarly, biomass pyrolysis products are also reported to be rich in oxygen content (Lu et al., 2009) which makes the fuel instable and corrosive (Garcıa-Perez et al., 2001). Hydrodeoxygenation and catalytic cracking are two commonly applied techniques to upgrade pyrolysis products (Zhang et al., 2007). Although fuel produced by hydrodeoxygenation is rich in hydrocarbons, the process itself is complicated and expensive. The catalytic cracking, on the other hand, is cheap but it enhances coke formation (8-25 wt.%). The technique for upgradation of pyrolysis oil should be cheap, effective, environmental friendly and simple (Bu et al., 2012).

One way to modify the quantity and quality of pyrolysis products is to use more than one type of feedstock mixed together for pyrolysis process and try to find out the optimum mix, giving improved products. Thus the process is also called co-pyrolysis. Co-pyrolysis technology is more desirable method in terms of ease of operation and design. Technically, the pyrolysis and co-pyrolysis processes are almost similar, as in both, experiments are conducted in controlled temperature in a reactor in the absence of oxygen (Abnisa et al., 2015). Synergistic effect is the main feature of this technique which occurs during co-pyrolysis reaction (Panda et al., 2010). Oil produced through co-pyrolysis of ST and biomass is more homogenous and stable as compared to the mixture of the oils produced by pyrolysis of the two feedstock separately. This is because oil from biomass is polar in nature and its mixture with ST oil is unstable as phase separation occurs within a short interval (Garcıa-Perez et al., 2001). Co-pyrolysis technique is termed as more promising, economic and environment friendly for waste disposal and energy production (Abnisa & Daud, 2015).

The present study was designed to explore the co-pyrolysis of SCB and ST with a focus on the quality and quantity of liquid yield as to the best of authors' knowledge, no work has been performed for oil production by co-pyrolysis of this feedstock combination. A fixed-bed reactor was used in the experiment. A total of fifteen experimental runs were performed, including three replicates each for SCB/ST ratios 1:0, 1:3, 1:1, 3:1 and 0:1 at 500 °C. The synergistic effect during the co-pyrolysis experiment was investigated by comparing the product yields and analyzing the oil samples for their physical and chemical properties using Elemental analyzer, Bomb calorimeter, Gas chromatography-Mass spectroscopy (GC-MS) and Fourier transform infrared spectroscopy (FTIR) etc.

1.2 Objectives of the study

- To study the potential of sugarcane bagasse as feedstock for pyrolysis oil.
- To observe whether a beneficial interaction from the co-pyrolysis of sugarcane bagasse and scrap tires in terms of oil quality and quantity.
- To characterized and compare liquid product obtained from pyrolysis and co-pyrolysis experiments.
- To investigate how much organic phase and aqueous phase are present in pyrolysis and co-pyrolysis oil obtained from the experiments.

1.3 Scope of the study

This study focused on the utilization of biomass waste and fossil based waste to fuels via pyrolysis technology. Therefore, all of the materials used in this study were collected from waste collection point. Sugarcane bagasse was collected from local sugar mills in Jhang city of Pakistan. Scrap tire was chosen as co-feed for the co-pyrolysis studies. The liquid was considered as the main product, whereas char and gas were referred as byproducts. Most of analyses were focused on the liquid product. The use of coals, catalysts, solvents, and any additional pressure in the co-pyrolysis process was beyond the scope of this study.

All the parameters such as temperature, particle size, reaction time, and nitrogen (N2) flow rate were set constant. The oil obtained from pyrolysis of sugarcane bagasse, scrap tire and co-pyrolysis of SCB/ST 1:3 were further characterization. All of experiments were performed using a fixed-bed reactor made of stainless steel.

CHAPTER 2

LITERATURE REVIEW

2.1 Co-pyrolysis process

Any technique to produce synthetic fuel should be simple and effective. Co-pyrolysis of lignocellulose biomass is a technique which possibly full fills both criteria. Two or more raw material as feedstock is used in this technique. From the literature it has proven that co-pyrolysis technique not only improves quality but it also improves quantity of liquid product. In contrast to other techniques such as hydrodeoxygenation and catalytic cracking, co-pyrolysis is more promising for industrial application because of its cost and performance.

The key to the success of this technique is the synergistic effect which occurs during co-pyrolysis reaction of two different feedstock. It is reported in the literature that oil from co-pyrolysis of biomass and scrap tire have high liquid yield and high calorific value compare to oil from pyrolysis of biomass alone.

The idea of mixing oils obtained from pyrolysis of biomass and pyrolysis of scrap tire is not possible as it may enhance oil cost. Polarity of the biomass pyrolysis oil makes it impossible to mix with scrap tire oil. The blend mixture of both oils remains unstable and easily separated in a short time interval. More energy is required for pyrolysis of biomass and scrap tire separately and it also enhance oil price. The co-pyrolysis process is a reliable method to produce homogenous oil compare to blending of oils individually. During co-pyrolysis experiments different radicals are interacted which favors the production of homogenous and stable oil (Juan D Martínez et al., 2014).

In addition, the main advantage of using co-pyrolysis technique is that the waste volume can be significantly reduced as waste is used as raw material. The advantages of this technique include solution of numerous environmental problems, less dependency on landfills, saving waste treatment cost etc. Moreover from economic point (Kuppens et al., 2010) reported that the technique of co-pyrolysis profitable compare to biomass pyrolysis alone and it has potential for industrial applications.

2.2 Mechanism of co-pyrolysis process

The process of pyrolysis and co-pyrolysis are almost similar, both process are performed without the presence of oxygen with moderate temperature in a closed reactor. The co-pyrolysis process comprise of three steps for the production of liquid yield which are; feedstock preparation, co-pyrolysis and finally condensation. Figure 2 shows the complete co-pyrolysis steps to produce liquid product. Before pyrolysis experiment, the feedstock should be dried either by sun drying or oven dry method. The objective of drying feedstock is to remove moisture content. High moisture in feedstock results in producing high water content in oil. A. V. Bridgwater (2012) reported that moisture should be less than 10% for pyrolysis process. Different studies suggested that other products of pyrolysis process such as char and gas can be used to produce heat for endothermic pyrolysis process as well as drying of feedstock (Venderbosch et al., 2010). The dried raw sample can easily be grinded, particle size less than 2 mm is required to attain high heating rate (A. V. Bridgwater, 2012).

2.3 Feedstock for the co-pyrolysis process

There are numerous renewable energy source around the world which includes; biomass, solar, wind and geothermal energy. But only the biomass can be converted into different types of fuels such as solid, liquid and gaseous using pyrolysis technology. Although oil obtained from pyrolysis of biomass have very low calorific value but it can be enhance using co-pyrolysis technique

2.3.1 Selection of feedstock

Co-pyrolysis of some biomass types has potential to enhance quantity and quality of liquid yield. Therefore biomass selection is very important. There are many different types of biomass which have been successfully used as feedstock for co-pyrolysis process which includes agricultural waste, dedicated energy crop, municipal solid waste and wood residue.

Table 1 shows different biomass types as feedstock used in co-pyrolysis studies, among all these waste, scrap tires is most common feedstock for co-pyrolysis studies. Scrap ties is mainly compose of rubber (65%) and black carbon 35 %. Oil obtained from scrap tire pyrolysis has calorific value of upto 44 MJ/kg which low oxygen content and contain aromatic and aliphatic compounds (Juan Daniel Martínez et al., 2013).

Table 1: Type of biomass used in co-pyrolysis process research to obtain liquid products

Types of biomass	**Biomass**
Agricultural waste	Pine nut shells (Uçar and Karagöz 2014), Cattle manure (Sánchez, Martínez et al. 2007), Corn stalk (Cordella, Berrueco et al. 2013), Corn residue (Aboyade, Carrier et al. 2013), Rice husk (Ye, Cao et al. 2008), Wheat straw (Ateş 2011), Pine cone (Brebu, Ucar et al. 2010)
Wood waste	Pine wood (Sharypov, Marin et al. 2002), Beech wood (Sharypov, Marin et al. 2002), Fir sawdust (Liu, Tian et al. 2013)
Municipal solid waste	sewage sludge (Samanya et al., 2012), recycled plastic (Pinto et al., 2013), polyethylene waste (Miranda et al., 2013), polystyrene waste (Abnisa et al., 2013), scrap tyres (Pinto et al., 2013), HDPE waste (Williams & Williams, 1997), PVC waste (Zevenhoven et al., 2002),
Dedicated energy crop	switchgrass (Weiland et al., 2012), willow (Cornelissen et al., 2008), Rapeseed (Samanya et al., 2012), sorghum (Cordella et al., 2013)

Table 2: Estimation of tire production for several countries in 2006 and 2007 (Ucar et al., 2005)

Countries	**Annual production (in thousand units)**	
	2006	**2007**
Brazil	42,216	N/A
Canada	30,216	33,303
China	274,230	336,700
France	59,000	61,300
Germany	75,342	75,218
India	32,880	33,695
Indonesia	41,300	44,300
Italy	32,017	31,140
Japan	175,916	176,207
Malaysia	11,560	13,420
Poland	28,931	30,747
Romania	14,761	16,600
Russia	40,417	42,330
South Korea	81,508	85,853
Thailand	26,931	N/A
Turkey	23,905	25,795
U.S	200,281	195,000

Petroleum is precious and limited source of energy, the day will come when petroleum will completely depleted from the world. But scrap tires are made from petroleum products which have same properties as fuel. Management of scrap tires required extra attention as it is precious energy source. A proportion of scrap tire can also be used for recycling. Utilizing scrap tire for production of oil should be reasoned. Therefore co-pyrolysis is a better option to utilize scrap tire as feedstock with other material.

2.3.2 Availability of feedstock

Availability of biomass is an important criterion for selecting biomass type. Biomasses easily fulfill this criterion as it is abundantly found all over the world. It can be acquired from agricultural residue, municipal solid waste, forestry residue, industrial waste, food processing waste, animal waste, sewage and agro-industrial waste. Therefore, as a result, the consumption of biomass is always high. Every country have different types of biomass which is depend upon different factors such as agricultural development, geographical conditions, industrial growth, population level, forest development, food demand, economic development, and lifestyle. Therefore every country has equal opportunity for co-pyrolysis process to obtain fuels from biomass.

Each year 1.5 billion tires produced around the world (Williams, 2013). Production of scrap tires in different countries in year 2006 and 2007 are shown in table 2. Around 64% scrap tires are illegally dumped, sent to landfill or stockpiled and only 13% of the scrap tires are recycled (Quek et al., 2013). Therefore extraordinary attention is required and co-pyrolysis was found effective, cheap, simple and environmental friendly.

2.4 Research on co-pyrolysis studies

It is important to explore different co-pyrolysis studies for developing idea of obtaining high quality oil from co-pyrolysis process. Therefore, different studies have been experimented by researched to investigate this technique and have reported many valuable findings. An overview of co-pyrolysis studies focusing liquid product are described below

2.4.1 Co-pyrolysis with scrap tires

Researchers are increasingly concerned with using scrap tires as fuel through pyrolysis processes. Research on different factors for the production of liquid fuel from pyrolysis are published in 2013 (Juan Daniel Martínez et al., 2013; Quek & Balasubramanian, 2013). There are several studies in the literature for pyrolysis of scrap tires and biomass separately and very limited on the blend. Therefore, it is important to investigate synergistic effect between different feedstock during co-pyrolysis with different pyrolysis parameters. Different studies for co-pyrolysis of biomass and scrap tires are brief in table 3.

Table 3: Co-pyrolysis studies with scrap tires

Classification	**Reference**	**Materials description**	**System Configuration and operating conditions**	**Relevant result and observations**
Co-pyrolysis of scrap tire with lignocellulose biomass	(Cao, Jin et al. 2009)	Crumb rubber obtained from scrap tire (ST) with particle size less than 0.17 mm blended with sawdust powder (SDP) having particle size (0.2-0.4 mm). The blend ratio ST/SDP 0:1, 2:3, 3:2 and 1:0 were performed.	Raw material of 100 g was used in fixed-bed reactor (FBR). The experiments were performed at 500 °C with heating rate of 20 °C/min. Nitrogen was purges for 30 minutes to extract out nitrogen present in the reactor.	The liquid product reached to 45%, 46.2%, 47% and 47.2 % at ST/SDP 0:1, 2:3, 3:2 and 1:0 into the blend ratio for feedstock. Pyrolysis oil obtained from pyrolysis of sawdust was 28.5 MJ/kg which was increased to 42.4 MJ/kg at ST/SDP 3:2 in the feedstock.
	(Alias, Hamid et al. 2011)	Scrap tires (ST) after removing steel cords were blended with empty fruit brunches (FB) at ST/FB 1:1	The experiments were performed in nitrogen atmosphere at temperature 500 °C in fixed-bed reactor. Oil was collected in the condensers.	The pyrolysis products obtained from the experiment were oil (42.8%, char (33.2%) and gas (24%) respectively, The pyrolysis oil was reduced when FB

				was pyrolyzed alone.
	(Önenc, Brebu et al. 2012)	Scrap tire after removing steel cords and textile netting was used in the experiment with particle size 1.5-2 mm. Oily sludge (OS) and bilge water oil (BW) were selected as feedstock.	Pyrolysis was performed at temperature 400 °C and 500 °C on individual ST, BW and OS and another experiment at temperature 500 °C with ratio BW/OS/ST 1:1:2.	The results showed that highest oil was obtained at temperature 500 °C. Oil obtained from pyrolysis of BW, OS and ST individually accounts 78, 71 and 39% respectively while for blend it accounted 51 %.

Cao et al. (2009) and Alias et al. (2011) reported that addition of scrap tire with biomass pyrolysis has considerably enhanced liquid yield and also increased the calorific value of the oil obtained. Önenc et al. (2012) investigated scrap tire co-pyrolysis with oily wastes and concluded that scrap tire and oily waste can be converted into valuable products using co-pyrolysis process which is an environmental friendly technique of converting hazardous waste into fuel.

2.5 Synergistic effects on co-pyrolysis

The main feature which is responsible for improving liquid yield quality and quantity is synergistic effect, which is consider as interesting area of study among the researchers. Several findings due to co-pyrolysis experiments are briefly explained in this section

2.5.1 Synergistic effects mechanism

Radical interactions of feedstock are responsible for synergistic effect during co-pyrolysis process. The positive and negative synergistic effect is dependent upon feedstock type and their contact, temperature and heating rate, catalysts, hydrogen source and solvent addition, pyrolysis duration and removal of volatiles formed. From all these factors blending raw material as feedstock is considerably persuade synergistic effect; hence synergistic effect for different studies can be changed (Fei et al., 2012).

There are several endothermic and exothermic reactions occur during pyrolysis of biomass (Demirbas, 2009), while pyrolysis of scrap tire involve radical mechanism (Önal et al., 2014).Önal et al. (2014) reported that synergistic effect is very difficult to understand as different chemical species are formed during co-pyrolysis, The author also reported that during co-pyrolysis of high density polyethylene different reaction radical can be formed which includes formation of monomers, formation of paraffin, formation of diens etc.

2.5.2 Increase in oil yield

The co-pyrolysis technique has potential to enhance liquid yield. Among the different factors which influence production of extra oil, biomass type is the crucial one. The quantity of liquid yield can be estimated when biomass undergoes through proximate analysis (Zhang et al., 2007). Volatile content and ash are important factors which have significant effect on quantity of pyrolysis oil. Volatile matter is converted into condensable vapors which get condensed into condensers (Asadullah et al., 2008). Ash content is responsible for increasing char and gasses while decreasing oil from the pyrolysis process (Fahmi et al., 2008; Venderbosch & Prins, 2010). Hence it is proven from the above studies that high volatile content and low ash benefits oil production from pyrolysis.

The volatile and ash content of scrap tire ranges between 57-75 % and 2-20% (Juan Daniel Martínez et al., 2013). In scrap tire polymeric compounds of synthetic and natural rubber are responsible for volatile matter. In a study (Ucar et al., 2005) showed that truck tire (TT) contains high volatile matter than passenger car tire (PCT). Author found more liquid yield from TT compare to PCT.

To enhance the production of condensable gasses from volatile matter, it is important to set all the process parameters accordingly. Temperature and heating rate are important parameters which have influenced on volatile matter (Guldogan et al., 2000), In another study Azeez et al. (2011) also reported that at temperature 450 °C and 500 °C almost all the volatile matters are obtained. In addition Pan et al. (1996) concluded that high heating rate favors high volatile yield from pyrolysis process.

2.5.3 Oil quality improvement

The quality of oil is also enhanced due to synergistic effect. The improvement in oil quality can be studied by fuel properties. The oil obtained from pyrolysis of biomass has very low calorific value due to high oxygen content. However calorific value of oil can be improved by co-pyrolysis process. It can be seen in the table 3 that oil obtained from co-pyrolysis experiment have increased calorific value. Juan D Martínez et al. (2014) reported that Carbon and Hydrogen content in liquid fuel is increase with the addition of scrap tire as feedstock while oxygen content decrease which significantly enhance heating value of the oil. Therefore, it is concluded that high fraction of scrap tire in biomass pyrolysis will considerably increase calorific value of oil.

Low energy density is due to high water content in liquid yield; thus, utilizing it as fuel, it is undesirable. Prior to pyrolysis, feedstock should be dried to remove moisture content which results in less water content in pyrolysis oil (Westerhof et al., 2007).

Viscosity is essential in designing chemical processing. The viscosity data is important for calculating pressure drop, mixing system consideration, heat transfer consideration and distillation calculations. Viscosity has influence on pumping and injecting of fuels. The viscosity of pyrolysis oil decreases as scrap tire increase in the feedstock (Cao et al., 2009).

Viscosity of oil can be reduced by mixing ethanol and methanol which is very easy and economic method to convert pyrolysis oil into stable fuels (Yu et al., 2007).

The major compounds formed in bio oil from pyrolysis of biomass are phenols, ketones, alcohols, acids, furans, aldehydes, and esters (Zhang et al., 2007). From all these compounds phenols is major compound in bio oil which is approximately 55% (Diebold, 2000). Instability and acidity of pyrolysis oil is due to high phenolic compounds (Samanya et al., 2012). These compounds are originated from lignin decomposition of biomass; lignin is also responsible for high viscosity and molecular weight of oil therefore one objective to improve oil quality is to eliminate phenolic compounds (Juan D Martínez et al., 2014). In a study, Juan D Martínez et al. (2014) while investigating biomass and scrap tire co-pyrolysis, the results showed that phenol compounds decreases with the addition of scrap tire in the feedstock blend. It concluded that phenolic compounds decrease because of synergistic effect during co-pyrolysis reaction.

The co-pyrolysis process is found to be an effective technique to recover hydrocarbon chemicals, which improves oil quality. These chemical can be determined using GC-MS and FT-IR analysis. In a study, Önal et al. (2014) reported an increase of 75 % alkenes fractions in co-pyrolysis oil compare to oil obtained from pyrolysis of biomass alone. In addition, Abnisa et al. (2014) reported that co-pyrolysis oil of palm shell and paper sludge contains benzene derivative of 33 % and aromatic compounds of 40% respectively.

Oil from biomass pyrolysis have very low sulfur content which is approximately 0.1 % (Abnisa et al., 2013), But with the addition of scrap tire as feedstock for co-pyrolysis process sulfur content increase in the pyrolysis oil. The technique of oxidative desulphurization is very effective to remove sulfur content from the oil (Ali et al., 2006).

2.6 Types of reactor used for pyrolysis

The type of reactors plays an important role in achieving the desired product distribution in pyrolysis process. Pyrolysis reactor designs include fixed beds reactor, fluidized bed reactor and circulating bed reactor.

2.6.1 Fixed-bed reactor

Fixed-bed reactor is a type of reactor device which contain feedstock material, typically in powder or pellet form, packed in a static bed. The syngas is then passed through the bed, where the reactions are induced as the gases contact the feedstock.

2.6.2 Fluidized-bed reactor

Fluidized bed reactor is a type of reactor device that can be used to carry out a variety of multiphase chemical reactions. In this type of reactor, a fluid (gas or liquid) is passed through a granular solid material at high enough velocities to suspend the solid

2.6.3 Circulating bed reactor

The circulating fluidized bed is a type of reactor which contains very fine particles which are fluidized at a rather high gas velocity, are blown out of the bed and reactor, and have to be replaced by fresh solids. We call these circulating beds.

2.7 Selection of reactor for co-pyrolysis process

The reactor type used for co-pyrolysis process has large function. In a study, A. Bridgwater (1999) showed that for successful co-pyrolysis process, a reactor should be capable of attaining short vapour resident time, high heating rate and moderate temperature to enhance liquid yield production, Numerous studies have been performed to explore reactor type to increase liquid production (Bridgwater, 2012; Isahak et al., 2012; Vamvuka, 2011; Venderbosch & Prins, 2010a, 2010b). Each reactor type has its own pros and cons in its operation and scaling. The fluidized bed reactor is easy to operate and scalability compare to other reactor types and it is best for fast pyrolysis. There are numerous studies in literature for co-pyrolysis studies in fixed-bed reactor (Abnisa et al., 2014; Cao et al., 2009; Liu et al., 2013; Önal et al., 2014). Fei et al. (2012) concluded that synergistic effect is the main feature of co-pyrolysis process which occur during contact of different feedstock at the time of co-pyrolysis technique, the author also concluded that positive synergistic effect is found in fixed-bed reactor compare to fluidized bed reactor.

Inert gas is used to carry condensable gasses from reactor to condensers for condensation process. Nitrogen is mostly used as inert gas because it is cheap compare to other gasses. Residence time of <2 second is required to limit secondary reaction into the reactor which enhance liquid product (A. V. Bridgwater, 2012). The inert gas is also depending upon reactor type. The circulating fluid bed reactor, fixed-bed reactor and entrained flow reactor requires high flow rates (Vamvuka, 2011).

2.8 Effects of process parameters on yield

In addition, the co-pyrolysis process is affected by different parameters which includes; biomass type, reaction time, temperature, feedstock size and heating rate. Akhtar and Amin (2012) discussed effect of different parameters to enhance liquid product for pyrolysis of biomass. In general 400-600 °C is the optimum temperature for the production of liquid product whereas less than 400 °C for char production and greater than 600 °C for production of gas. However optimum temperature to enhance liquid product depends upon feedstock type therefor thermogravimetric analysis can be performed to understand thermal behavior of the feedstock (Velghe et al., 2011).

Co-pyrolysis process has a unique parameter compare to normal pyrolysis which is mixing ratio of raw material. The ratio of different feedstock is very significant to enhance production of liquid yield. Sharypov et al. (2002) reported biomass to scrap tire ratio in feedstock is the most significant parameter to enhance liquid yield production.

2.9 Co-pyrolysis process by-products

Co-pyrolysis also produces other by-products such as char and gas. A. V. Bridgwater (2012) reported that from dried feed char produced from biomass pyrolysis is upto 12 % whereas gas accounts 13% respectively. Calorific value of gas is very low as compare to natural gas which can be enhanced by co-pyrolysis technique.

This review showed that many researchers have studied the potency of co-pyrolysis technique using various types of biomass wastes, and that the results are very encouraging. Different investigations were conducted to obtain oil with a high yield and high quality, which followed the various available standards. Several advantages can be obtained from using this technique such as reducing the consumption of fossil fuels, solving some environmental problems, increasing energy security, and improving waste management systems. Apart from these, this technique also offers simplicity in design and feasibility in regard to economic analysis.

There are some important factors which need to be highlighted in the feed system of the co-pyrolysis process. To obtain a high-grade liquid, adjustments of the types and ratios of feedstock are essential. The suitable combination of feedstock in co-pyrolysis can include wood-based biomass with waste plastic or wood-based biomass with waste tyre.

Both options are acceptable, since many studies have proven that these combinations can provide improvements in the pyrolysis oil through synergistic effects.

Co-pyrolysis is a promising technique that can produce a high grade pyrolysis oil from biomass waste. This technique also offers several advantages on its application:

- Co-pyrolysis can be easily applied to existing plants of the pyrolysis of biomass.

- The low cost associated with upgrading processes from pyrolysis to co-pyrolysis: if a plant is run for the pyrolysis of wood-based biomass, there will be no need to invest money in a special plant for the use of waste plastics and tyres.

- No special equipment needs to be designed and constructed for co-pyrolysis. Some minor modifications maybe needed, but only for the feed preparation system.

- As a byproduct, solid fuel is sometimes poor in organic matter; the addition of waste plastics and tyres to wood-based biomass may improve its quality.

- The quantity and quality of desired products (oil, solid or gas) can be easily controlled by adjusting process parameters.

The primary disadvantage of co-pyrolysis lies in the biomass preparation unit. Given that this technique deals with many types of biomass, an additional pre-treatment system is required, which can substantially increase the cost for the installation and operation of such units.

CHAPTER 3

METHODOLOGY

Details about materials and methods are described in this chapter, which were used for the investigation purpose of the study. Research work was performed in synthesis laboratory of USPCASE, NUST and Environmental Chemistry laboratory of IESE, NUST. Following sections represent the detail of specific experiments and all conditions of this study.

3.1 Experimental Setup

Co-pyrolysis of SCB and ST was carried out in fixed-bed reactor constructed of stainless steel with length, internal and external diameters of 50.8, 10.8 and 11.4 cm respectively and a 0.6 cm external diameter outlet tube at the reactor top. The fixed-bed reactor was attached with two condensers, utilizing tap water (approximately 20 °C) and ice water (added with NaCl, -2 to -5 °C) to liquefy the condensable pyrolysis products. A Proportional-Integral-Derivative (PID) controller was used to control the heating rate with K-type thermocouple for temperature motoring.

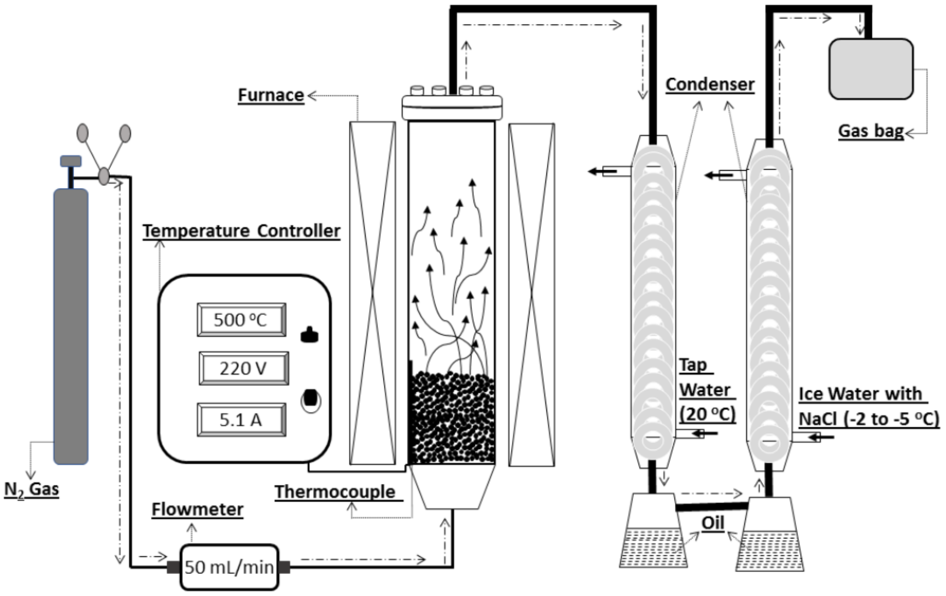

Figure 2: Schematic diagram of pyrolysis or Co-pyrolysis process

For each run of the experiment, 200 g of sample was fed into the fixed-bed reactor which was then sealed and heated from ambient temperature at a constant rate of 20 °C/min, up to 500 °C. The temperature was maintained at 500 °C for 30 minutes. Before starting to heat up the sample, air in the reactor was purged with nitrogen gas flowing at the rate of 50 mL/min, Nitrogen flow was continued throughout the experiment to carry the gaseous pyrolysis products.

3.2 Experimental Conditions

The reactor was operated with different operating condition which was found from different analysis and literature. The main operating parameter was SCB/ST blend ratio, the experiments were performed at SCB/ST 1:0, 3:1, 1:1, 1:3 and 0:1 followed by temperature and heating rate which was maintained at 500 °C and 20 °C/min. Sample size 200g, nitrogen flowrate 50 mL/min, particle size 0.6-1.6 mm and two condensers one with tap water and other with ice water (ice and NaCl)

3.3 Feedstock preparation and characterization

Sugarcane bagasse was collected from local sugar mills in Jhang city of Pakistan with initial moisture content of 47 wt.% which was reduced to less than 10 wt.% by sun drying. Sugarcane bagasse was milled and sieved to obtain uniform particle size between 0.6-1.8 mm. The component analysis of Sugarcane bagasse samples was carried out according to the method reported in literature (Li et al., 2004). Scrap tire was obtained from a rubber recycling vender in Rawalpindi-Pakistan. Textile netting and steel cords in ST were removed by vendor which was then grinded and sieved to obtain uniform particle size of 0.6-1.8 mm. Physico-chemical properties of Sugarcane bagasse and Scrap tire samples were determined by proximate analysis according to ASTM D3172-07. Elemental analyzer (LECO CHNS 932) was used to determine elemental composition of raw samples according to ASTM D5291-96. Bomb calorimeter (LECO AC-350) was used to determine calorific values of raw materials according to ASTM D 240.

The thermal degradation of lignocellulosic sample may lead to several reactions. Therefore, it is important to pre-study the thermal degradation of the sample with respect to temperature in order to assess optimum parameters of thermochemical process to convert biomass into energy products (Damartzis et al., 2011). In this study, Thermogravimetric analysis (TGA) was used to understand thermal behavior of the sample. Optimum temperature for maximum liquid yield was also determined by TGA.

TG analyzer (Mettler Toledo) was used for TGA of SCB and ST with a sample mass of 4.2 mg and 5.3 mg respectively in nitrogen atmosphere, The sample was heated at a constant heating rate of 20 °C/min from ambient temperature to 617 °C with 20 mL/min of gas flow rate.

3.4 Product Characterization

As per mentioned scope, the study was focused on liquid yield of pyrolysis and co-pyrolysis with gases and char as by products. Samples of liquid yields, once separated from aqueous phase, were characterized for multiple parameters following respective ASTM methods to determine their physical and chemical properties. Oil samples of the feedstock combinations giving highest yield were analyzed in more details.

3.4.1 Physical analysis of product

The kinematic viscosity, flash point and specific gravity of the liquid yield were tested according to ASTM D445, ASTM D7236 (Setaflash Series 3) and ASTM D4052-96 respectively whereas pH was determined with a digital pH meter (Hach sensION 156). Elemental analyzer (Thermo Scientific FLASH 2000) was used to determine elemental content of oil according to ASTM D5373. Calorific values were calculated by bomb calorimeter (LECO AC-500) according to ASTM D240.

3.4.2 Chemical analysis of product

FTIR is an appropriate analytical technique to understand structural and compositional changes during pyrolysis and co-pyrolysis. Bruker Alpha FTIR was used to determine organic functional groups of chemicals present in the pyrolytic oil at 2 cm^{-1} resolution in the range of 550–4000 cm^{-1}. The scanning of infrared spectrum was performed by a small drop of bio oil mounted on pellet.

The GC-MS analysis of the obtained pyrolytic oil samples was performed by Shimadzu QP2020 with QP series mass selective detector. An SH-Rxi-5Sil Ms capillary column was used having length of 30 m, diameter 0.5 mm, and fused silica capillary with a film thickness of 0.25 μm. The GC initial oven temperature was 40 °C for first 5 minutes and was programmed to increase 175 °C at a heating rate of 3 °C/min followed by a hold for 5 minutes there and then to 200 °C at a heating rate of 5 °C/min. The temperature was held there for 5 minutes; and was further raised to 250 °C at a rate of 5 °C/min followed by a hold for 5 minutes. Mass selective detector QP series ion source was used at the end of the column. The data acquisition system was completed with G1035A software using a NIST library database.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Feedstock characterization

4.1.1 Thermogravimetric analysis

The TGA results of SCB and ST are shown in Figure 3. Both materials showed loss of weight with increase in temperature. Decomposition started earlier for SCB because of its low thermal stability at 200 °C whereas ST started to decompose at temperature around 300 °C. SCB is mainly composed of lignocellulose and moisture content therefore, its pyrolysis is characterized into three stages of decomposition (Wang et al., 2008) whereas pyrolysis of ST has only one decomposition stage as ST is composed of long-chain polymer (Raj et al., 2013). The first stage of SCB decomposition occurred from room temperature to 136 °C with 8.5 wt.% weight loss, followed by second stage, from 200 °C to 380 °C with maximum weight loss of 53.4% and the final stage ranged from 380 °C to 480 °C with weight loss of 12.9%. Williams et al. (1993) reported that during first stage moisture and extractives are released. Decomposition of cellulose and hemicellulose is associated with the second stage. Lignin is decomposed in final stage due to its complicated structure. In case of ST, decomposition occurred in temperature range of 300-480 °C with maximum weight loss of 41.3%, associated with the decomposition of natural rubber as well as mixture of butadiene and styrene-butadiene rubbers (Murillo et al., 2006). White et al. (2011) reported that depolymerisation reaction occurs in temperature range of 280-500 °C which results in production of liquid yield containing various organic compounds. In case of ST, most of the weight loss was observed till 500 °C and beyond that it was negligible. It can be concluded from the TGA results as well as previous reports that 500 °C is the optimum temperature for co-pyrolysis of ST and SCB.

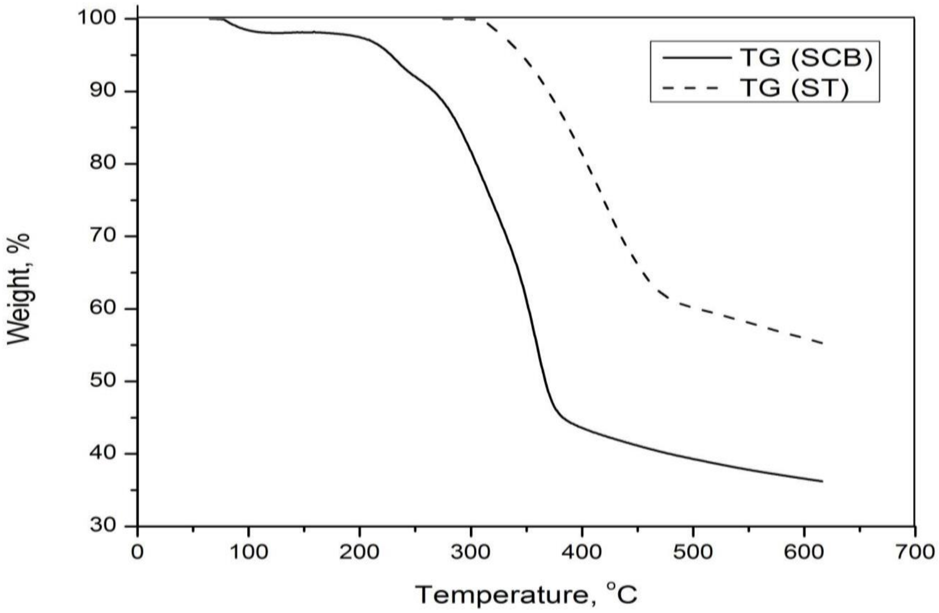

Figure 3: TGA Plot of SCB and ST

4.1.2 Proximate and ultimate analysis

The results of proximate, ultimate, component and calorific value analysis are shown in figures 4, 5, 6 and 7.

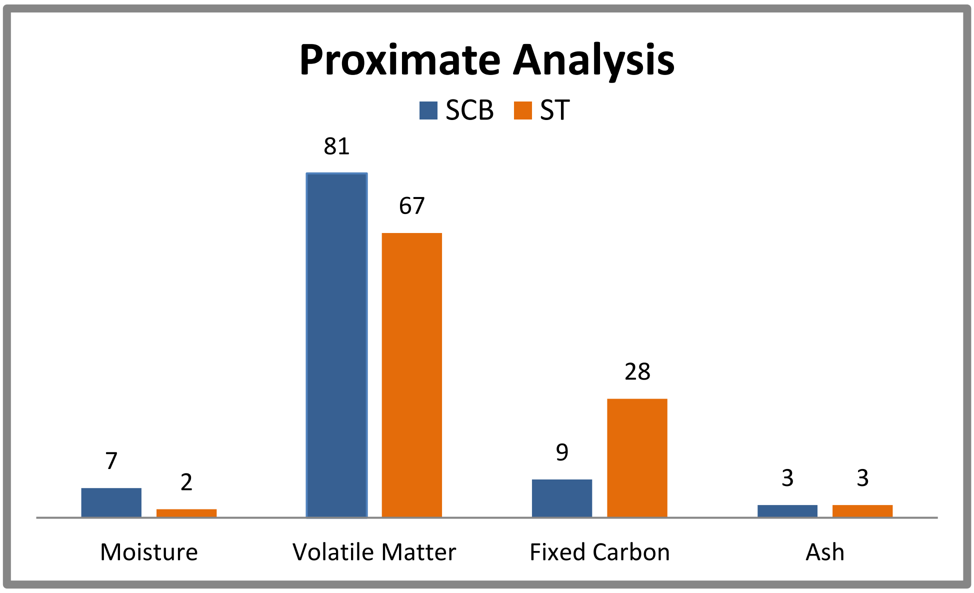

Figure 4: Proximate analysis of sugarcane bagasse and scrap tire

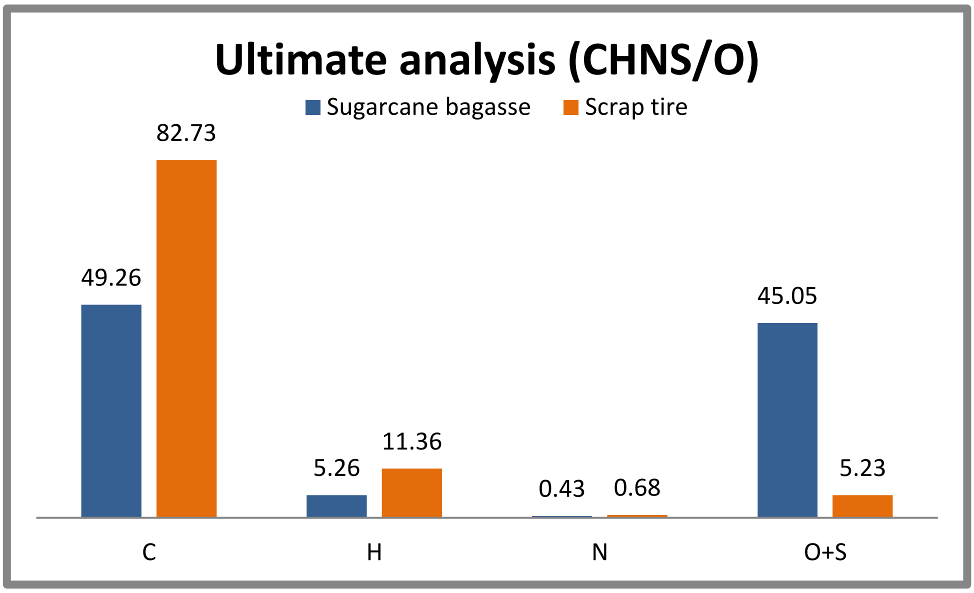

Figure 5: Ultimate analysis of sugarcane bagasse and scrap tire

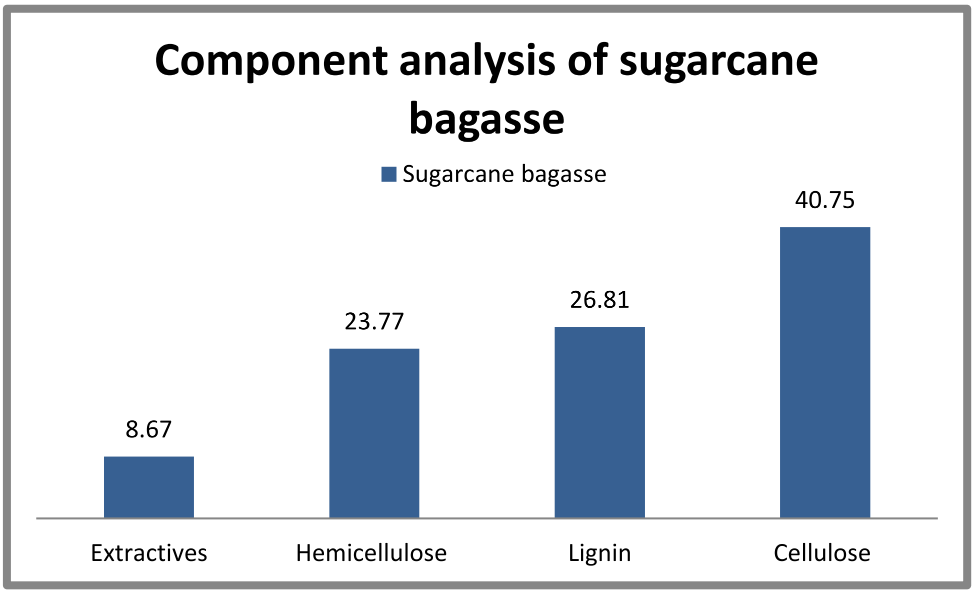

Figure 6: Component analysis of sugarcane bagasse

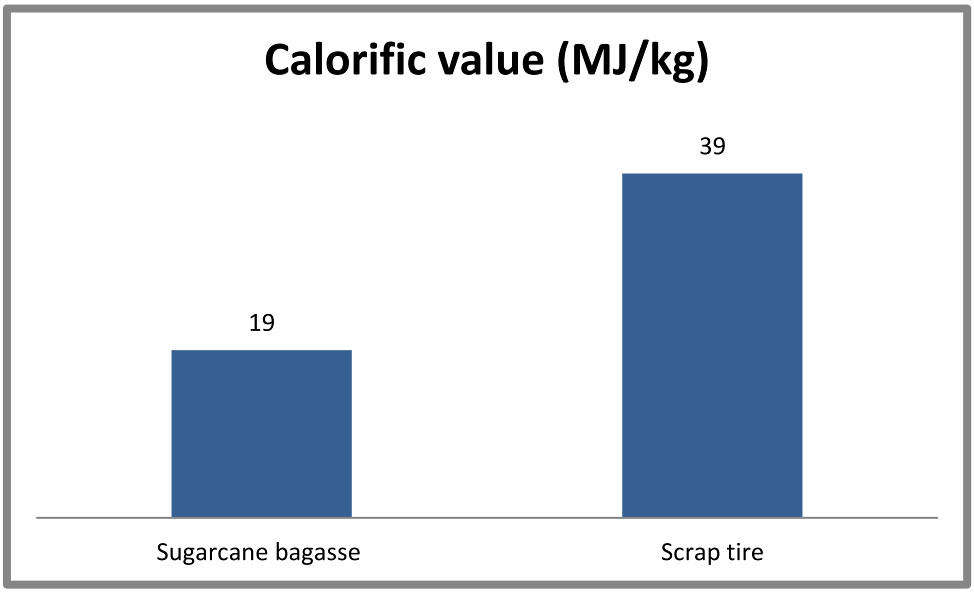

Figure 7: Calorific value of sugarcane bagasse and scrap tire

Ash content and volatile matter of the feedstock are two important factors in determining the quantity and quality of pyrolytic oil. It has been reported that pyrolysis liquid yield decreases due to the presence of high ash content which also contributes to the production of non-condensable gases and char (Asadullah et al., 2008). Whereas higher volatile matter content results in higher quantity and quality of liquid pyrolytic yield (Fahmi et al., 2008). Moisture content in biomass enhances the production of AP in pyrolysis liquid, which not only reduces its calorific value but also decreases conversion efficiency. Proximate analysis results showed that volatile matter was 81.2 wt.% and 66.7 wt.% in SCB and ST respectively, indicating higher energy potential of the feedstock. Ultimate analysis results showed higher percentage of Carbon and Hydrogen in ST as compared to SCB, as expected because of its origination and indicates its high potential for conversion into hydrocarbon fuels. The higher oxygen percentage in the material may deteriorate its heating value (Abnisa et al., 2013). Hence ST has high calorific value. ST is hydrogen rich rubber having 11.3% hydrogen content as compared to 5.3% of SCB. Higher hydrogen percentage in ST enhances the product yield (Ucar et al., 2005).

4.2 Product characterization

4.2.1 Product composition

Pyrolysis yields of SCB, ST and their mixtures with different ratios are shown in Figure 8.

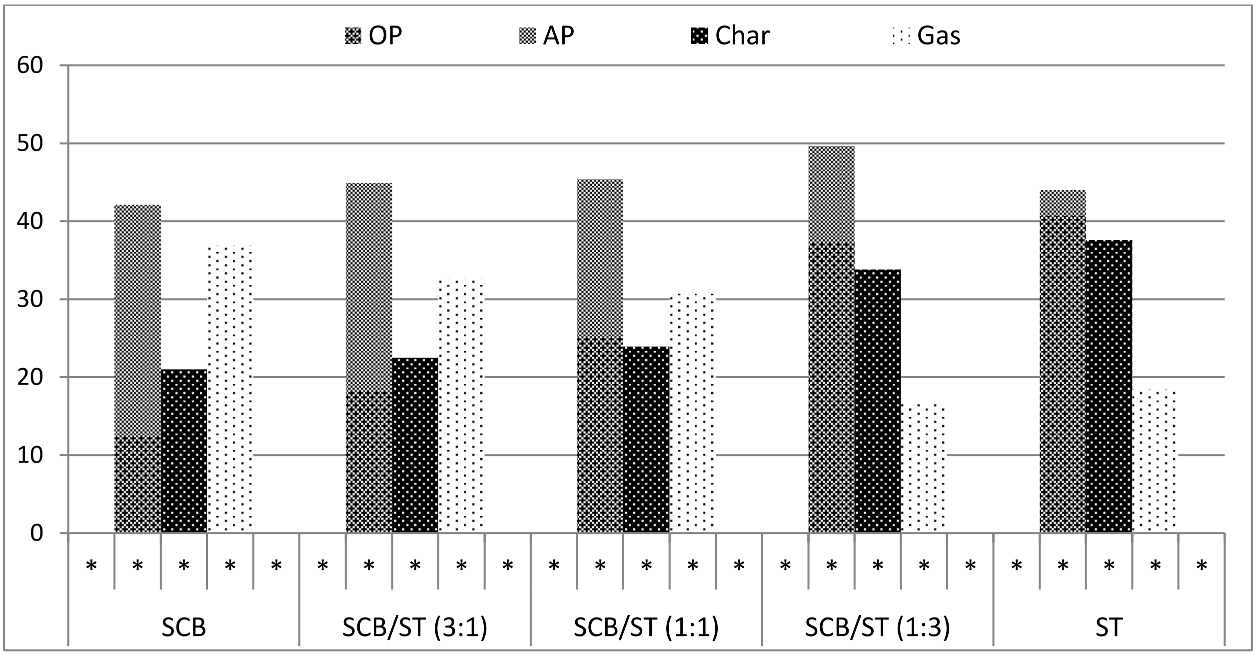

Figure 8: Product Distribution from pyrolysis of SCB and ST and their mixture

The liquid product obtained from this study was higher as compared to char and gas. The gas yield was found to be the lowest in the range of 16.5 to 36.8 wt.% with lowest value for SCB/ST 1:3.

Liquid oil yield increased with increase of ST in the blend. The pyrolysis of SCB alone produced approximately 42.1 wt.% of the pyrolysis oil. As the ST composition in the blend increased from 3:1, 1:1 to 1:3 in the reaction, the liquid yield also increased to 44.9, 45.4 and 49.7 wt.% respectively. The maximum pyrolysis oil was produced from mixing ratio of SCB/ST 1:3 indicating the highest synergistic effect among the tested blend ratios. However, it can be seen in the Figure 8 that as ST in the co-pyrolysis increased, AP yield decreased subsequently. The same trend was observed by Cao et al. (2009) while studying co-pyrolysis of sawdust and waste tires . As waste tires have higher hydrogen content than biomass, during co-pyrolysis reaction it provides more hydrocarbons resulting in increase in liquid product yield (Ucar et al., 2005).

Similar to liquid yield, char production from the co-pyrolysis increased with increase in ST in the blend. This trend can be explained by the presence of higher proportion of fixed carbon in ST and lower volatile matter compared to SCB (Figure 4). As the ratio of ST in the feedstock increases, it enhances the production of char yield. The char from the pyrolysis of SCB was 21 wt.% which increased to 33.8 wt.% for SCB/ST 1:3. Previously, Juan D Martínez et al. (2014) have also reported similar results, explaining that as compared to lignocellulosic biomass, ST comprise of higher fixed carbon and lower volatile matter which gives rise to the formation of char in the co-pyrolysis of biomass and ST.

In present study pyrolysis of ST produced 44 wt.% liquid yield which can be comparable to literature (de Marco Rodriguez et al., 2001). Similarly, liquid yield produced from SCB was 42.1 wt.% which was within the 34 to 75 wt.% range earlier reported (Akhtar & Amin, 2012).

4.2.2 Liquid yield characterization

Results of elemental analysis, calorific value, kinematic viscosity, specific gravity, flash point and pH of ST, SCB pyrolysis oil and SCB/ST 1:3 co-pyrolysis oil experiments are shown in Figure 9, 10, 11, 12, 13 and 14. The properties of SCB/ST 1:3 oil was considerably improved. The elemental analysis showed that carbon content in SCB/ST 1:3 co-pyrolysis oil increased to 85.3% due to addition of ST into SCB and oxygen content decreased to 4.1%. Hydrogen content was also increased to 9.9% in co-pyrolysis oil. Calorific value of SCB was 19.1 MJ/Kg which was increased to 41 MJ/kg in co-pyrolysis oil of SCB/ST 1:3 blend which is almost equal to calorific value of ST. It can be concluded from the results that SCB/ST 1:3 co-pyrolysis oil was improved due to ST addition.

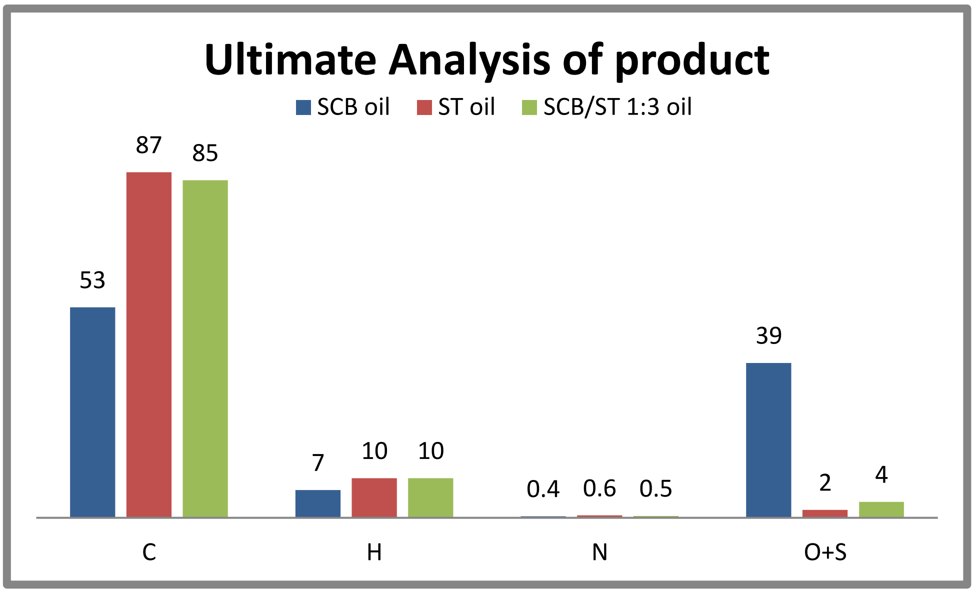

Figure 9: Ultimate analysis of SCB, ST and SCB/ST 1:3

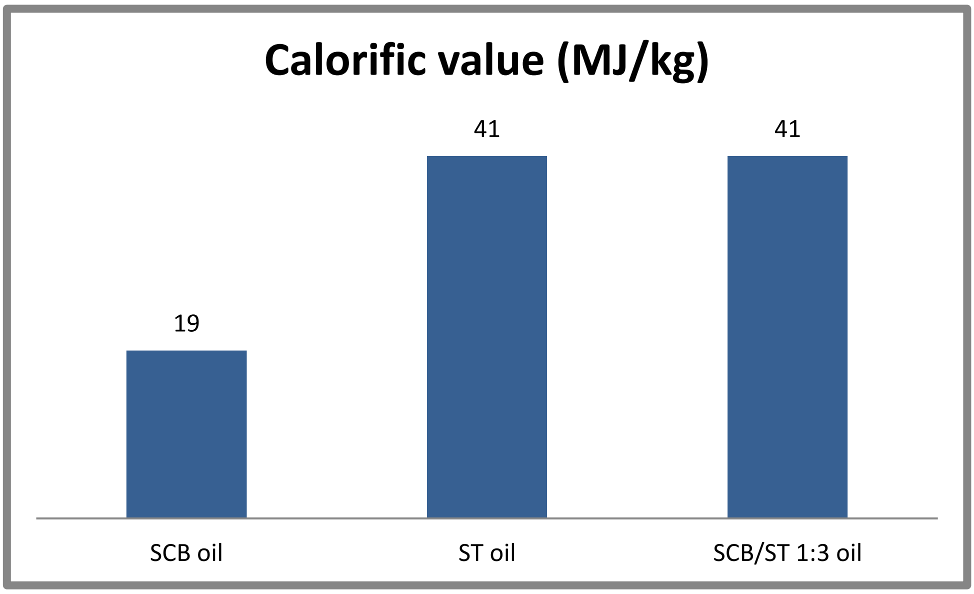

Figure 10: Calorific value analysis of SCB, ST and SCB/ST 1:3

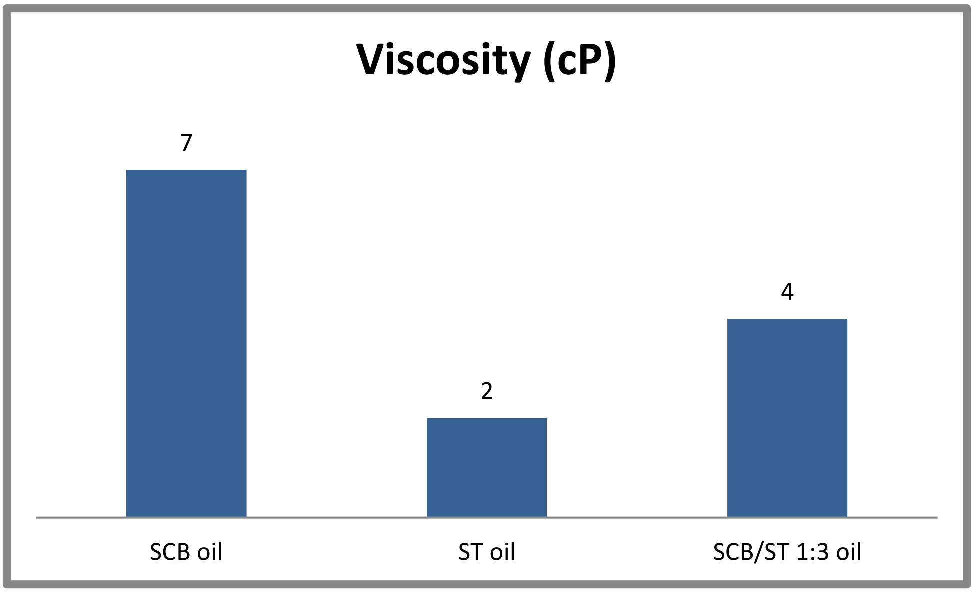

Figure 11: Viscosity of SCB, ST and SCB/ST 1:3

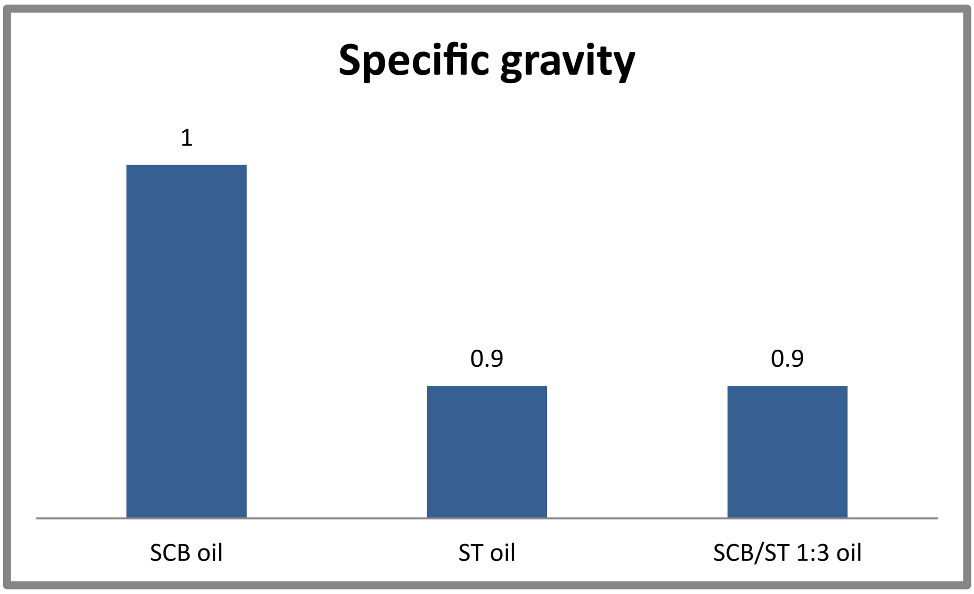

Figure 12: Specific gravity of SCB, ST and SCB/ST 1:3

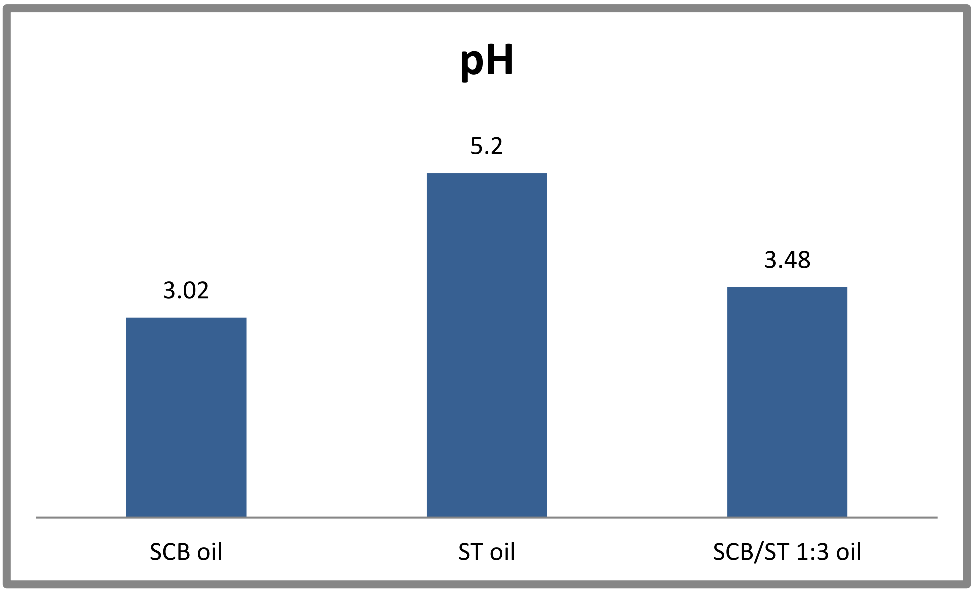

Figure 13: pH of SCB, ST and SCB/ST 1:3

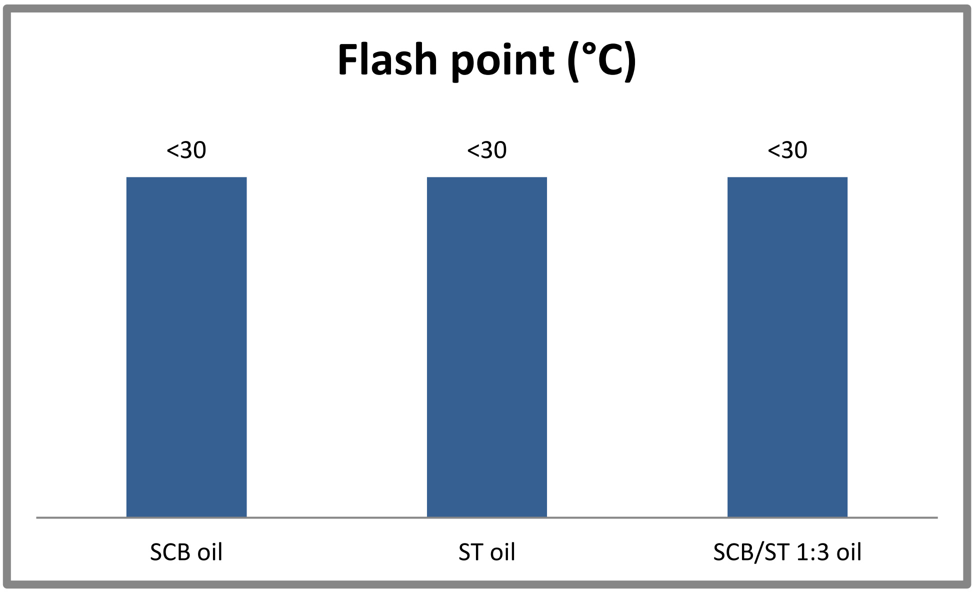

Figure 14: Flash point of SCB, ST and SCB/ST 1:3

4.2.3 FTIR analysis

Table 4 illustrates the results of the functional group analysis of SCB, ST pyrolysis and SCB/ST 1:3 co-pyrolysis oils. The FTIR spectrum of co-pyrolysis oil was found to be similar to ST oil, as depicted in Figure 15. However, SCB pyrolysis oil showed numerous additional peaks at different wavenumbers, corresponding to the presence of additional/different functional groups in the sample. The additional functional groups disappeared in the co-pyrolysis oil which can be attributed to the fact that ST contains more hydrogen content compared to SCB (Figure 5) and during co-pyrolysis process ST plays an important role as a hydrogen content source (Ucar et al., 2005). Most alkynes present in ST pyrolysis oil are also present in co-pyrolysis oil and are not found in SCB pyrolysis oil. As consequence, it is inferred that, during SCB/ST co-pyrolysis, alkenes changed to saturated hydrocarbons. Co-pyrolysis and ST oils are mostly comprised of aliphatic compounds with small amounts of aromatic compounds (i.e phenols, esters, alkane, alkene, alkyne, alcohols and others (Abnisa et al., 2013). Similarly aldehydes present in SCB pyrolysis oil are absent in co-pyrolysis oil samples. This can be explained by the fact that in acidic conditions, phenolic compounds are inclined to polymerize with aldehydes (Sharma et al., 2003). Therefore due to synergistic effect, the pyrolysis oil obtained is more stable having lesser aldehyde content. Moreover, SCB oils showed significant peak area corresponding to 3200-3600 cm^{-1}, indicating presence of phenols and alcohols presumably consequent of the higher lignin content of SCB. Lignin derived products are normally long chain (higher molecular weight) and causing higher viscosity of oil, a characteristic unwanted for fuels and thus needs further treatment to upgrade the fuel combustion characterizes. Peaks for both, ST and co-pyrolysis samples showed decreased areas for corresponding to t phenols and alcohols, showing improved fuel quality due to synergistic effect. It can be concluded that addition of ST in SCB improved the quality of pyrolysis oil produced.

Table 4: FTIR analysis of product

Type of Functional Group	**Wave number, cm-1**	**Class of Compound**	**SCB**	**ST**	**SCB/ST (1:3)**
O–H stretching	3,600–3,200	Phenols, alcohols	✓	×	×
C–H stretching	3,000–2,800	Alkanes	✓	✓	✓
C=O stretching	1,780–1,650	Ketones, aldehydes, carboxylic acids	✓	×	×
C=C stretching	1,630–1,590	Alkenes	×	✓	✓
C–H bending	1,465–1,350	Alkanes	✓	✓	✓
C–O stretching O–H bending	1,300–950	Primary, secondary and tertiary alcohols, phenols	✓	✓	✓
C–H bending	900–650	Aromatic compounds	✓	✓	✓

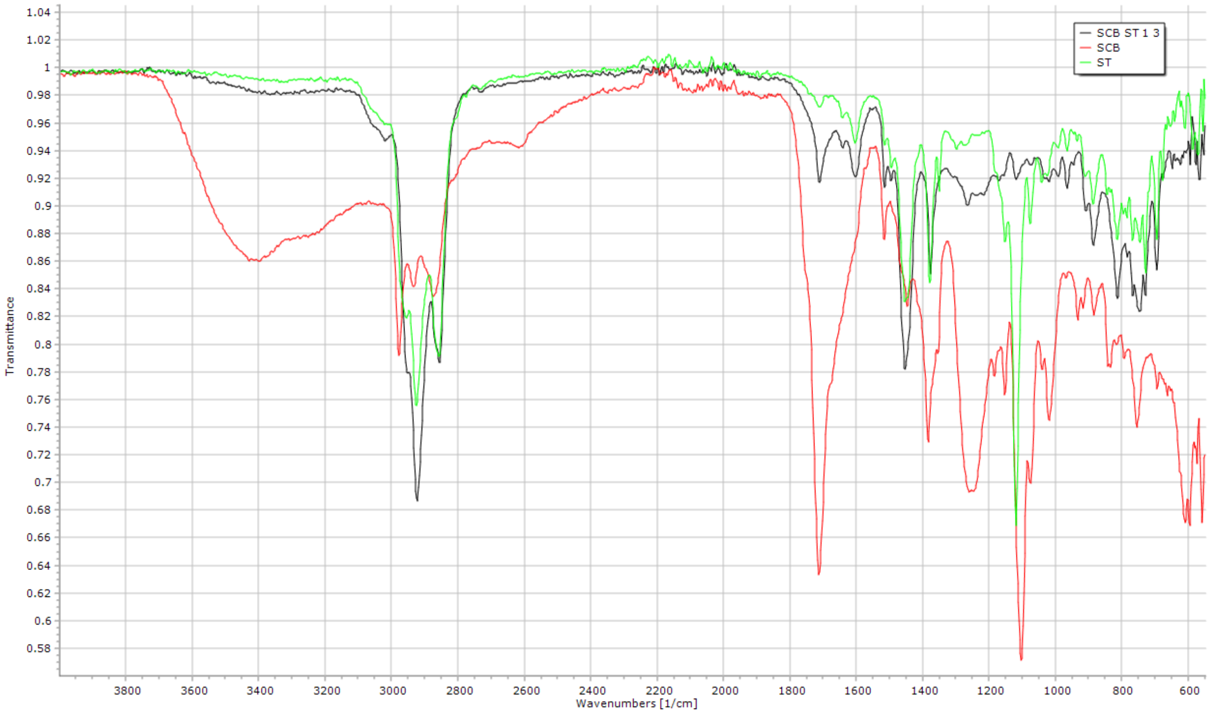

Figure 15: FTIR spectrum of product

4.2.4 GC-MS analysis

Liquid yields of SCB, ST and their blend ratio 3:1 were analyzed by GC-MS and their major compounds are presented in Table 5. The results showed presence of carbon distribution ranging from C_3 to C_{30}. More long-chain hydrocarbon were found in co-pyrolysis oil, in addition to those found in ST oil which indicates that the synergistic effect has promoted the formation of saturated hydrocarbons. Similar trend was observed in previous studies (Bhattacharya et al., 2009).

Table 5: GC-MS analysis of product

S.No.	**R.T. (min)**	**Name of Compounds**	**Chemical Formula**	**% Area**		
				SCB	**ST**	**SCB/ST (1:3)**
Benzene derivatives						
1	3.75	Methylbenzene	C_7H_8		12.5	3.8
2	7.01	Ethylbenzene	C_8H_{10}		2.8	1.3
3	7.4	1,4-Dimethylbenzene	C_8H_{10}		11.5	4.7
4	12.17	1-ethyl-2-methyl-Benzene	C_9H_{12}		2.5	1.7
5	12.85	1,2,3-trimethyl-Benzene	C_9H_{12}		9.1	4.2
6	13.86	alpha.-Methylstyrene	C_9H_{10}		1.2	
7	16.01	1,2-propadienyl-Benzene	C_9H_8		2.3	
8	20.14	2,4-Dimethylstyrene	$C_{10}H_{12}$		2.2	1.1
9	26.46	2-cyclopropylethenyl-Benzene	$C_{11}H_{12}$		1.1	
Phenols						
10	13.06	Phenol	C_6H_6O	14.5		1
11	17.39	2-Methylphenol	C_7H_8O	12.9		0.9
12	18.31	2-Methoxyphenol	$C_7H_8O_2$	2.8		
13	21.98	2,5-Dimethylphenol	$C_8H_{10}O$	2.7		

S.No.	R.T. (min)	Name of Compounds	Chemical Formula	% Area		
				SCB	**ST**	**SCB/ST (1:3)**
14	23.47	2-Methoxy-5-Methylphenol	$C_8H_{10}O$	1.2		
15	23.81	1,2-Benzenediol	$C_6H_6O_2$	5		
16	24.99	Benzothiazole	C_7H_5NS	1.2	1.5	1.4
17	26.75	3-Methyl-1,2-Benzenediol	$C_7H_8O_2$	2.4		
18	27.52	4-Ethoxyphenol	$C_8H_{10}O_2$	3.4		
Terpenes						
19	13.73	D-Limonene	$C_{10}H_{16}$		17.1	8.4
Olefins						
20	3.44	3-Methyl-2,4-hexadiene	C_7H_{12}		1.1	
21	4.11	1,3,6-Heptatriene	C_7H_{10}		0.9	
22	4.45	(E)-3-Undecene	$C_{11}H_{22}$		0.8	
23	5.57	1,2-dimethyl-Cyclohexene	C_8H_{14}		1.1	
24	5.95	4-ethenyl-Cyclohexene	C_8H_{12}		2.6	1
25	8.42	1-ethynyl-1-Cyclohexene	C_8H_{10}		5.2	2.5
26	9.36	3,4-dimethyl-1,5-Hexadiene	C_8H_{14}	2.9		1.1
27	12.73	7,7-dimethyl-1,3,5-Cycloheptatriene	C_9H_{12}		1.2	1.3

S.No.	**R.T. (min)**	**Name of Compounds**	**Chemical Formula**	**% Area**		
				SCB	**ST**	**SCB/ST (1:3)**
28	15.47	4-ethenyl-1,4-dimethyl-Cyclohexene	C10H16	1.9		0.8
29	16.82	3-bromo-1,5-Cyclooctadiene	C8H11Br		0.9	
30	16.92	3,7,7-trimethyl-1,3,5-Cycloheptatriene	C10H14		0.8	1
31	17.95	3-ethylidene-2-methyl-1-Hexen-4-yne	C9H12		1	1.1
Alkanes						
32	3.84	Methylene-Cyclohexane	C7H12		0.9	
33	45.23	Heptadecane	C17H36			2
34	37.59	Tetradecane	C14H30			1.5
35	48.78	Pentadecane	C15H32			0.9
36	75	1-iodotriacontane	C30H61I			0.3
Aldehydes and ketones						
37	2.29	(R)-(-)-2-Amino-1-propanol	C_3H_9	1.4		
38	3.22	1-methyl-3-Cyclohexen-1-ol	C7H12O	1.8		
39	5.89	Furfural	C5H4O2	3.1		
40	6.86	2-Furanmethanol	C5H6O2	4.2		2.5
41	7.63	1-(Acetyloxy)-2-propanone	C5H8O3	3		

S.No.	R.T. (min)	Name of Compounds	Chemical Formula	% Area		
				SCB	ST	SCB/ST (1:3)
42	11.96	5-Methylfurfural	C6H6O2	4.5		
43	12.44	2,3-Pentanedione	C5H8O2	1.4		
44	13.01	cis-1,2-Dihydrocatechol	$C_6H_8O_2$		1.2	
45	15.11	2-hydroxy-3-methyl-2-Cyclopenten-1-one	C6H8O2	3.5		1.3
46	15.81	2,3-dimethyl-2-Cyclopenten-1-one	C7H10O	2.2		1
Polycyclic aromatic hydrocarbon (PAH)						
47	23.01	Naphthalene	C10H8	1.1		2.1
48	28.27	1,4-dihydro-1,4-Methanonaphthalene			1.7	
49	28.61	1-Methylnaphthalene	C11H10	1.2		4.5
50	33.46	2,3-dimethylnaphthalene	C12H12			6.1
51	34.27	2,3,6-trimethylnaphthalene	C13H14			2.4
52	34.63	1-(2-methylphenyliminomethyl)-Naphthalene-2-ol			1.6	
53	38.52	1,2-dihydro-6-methyl-Naphthalene	C11H12			4.1
Acids and acid derivatives						
54	2.298	Alanine	C3H7NO2	1.2		

S.No.	R.T. (min)	Name of Compounds	Chemical Formula	% Area		
				SCB	ST	SCB/ST (1:3)
55	4.75	2-Nonynoic acid			1.3	1
56	25.24	2,5-Dimethyl-2,4-hexadienedioic acid	$C_8H_{10}O_4$	6.3		
57	30.77	Formic acid, 2,6-dimethoxyphenyl ester	$C_9H_{10}O_4$	3.6		

As shown by FTIR peaks, GC-MS also confirmed that OP of SCB oil contained number of aliphatic and aromatic compounds with a significant proportion of phenol and its derivatives (51%) which are mainly formed from the decomposition of lignin part of the biomass (Kim et al., 2010). More precisely, phenol and 2-methylphenol were observed as the major compounds in SCB oil. Aldehydes and ketones were the second most significant (30%) group of compounds in the SCB pyrolysis oil. Major Identified compounds in ST oil were from benzene derivatives (48%) and terpenes group (17%). Previous studies involving pyrolysis of scrap tires have reported the presence of similar amounts of limonene and attributed their formation to the thermal decomposition of natural rubber (polyisoprene) (Pakdel et al., 2001). Similarly, Ucar et al. (2005) have compared the pyrolysis products of passenger car scrap tire with that of trucks. The results showed that formation of benzene derivatives varied between the two tire types, with passenger car tires showing significantly higher amount of benzene derivative, similar to the results found in our study.

Less than 2% phenol group compounds were found in ST oil which was reflected in the co-pyrolysis oil by their low proportion. Overall, composition of the co-pyrolysis oil resembled that of ST. Benzene derivatives and PAHs with 19% each composition were most significant part of the co-pyrolysis oil followed by D-limonene (8%). Higher amount of benzene derivative and D-limonene in co-pyrolysis oil is attributed to their abundance in ST oil. However, PAHs were neither significantly detected in SCB nor ST oils. Sharma and Hajaligol (2003) investigated the effects of pyrolysis conditions on the formation of PAHs and discussed a stepwise mechanism of the formation of larger PAH molecule from smaller molecules of phenol during pyrolysis process. As the co-pyrolysis oil showed much smaller fractions of phenol as compared to SCB oil, higher amount of PAHs in the co-pyrolysis oil are attributed to the synergistic effect causing the formation of PAHs according to the reported mechanism. . Similar trends in the results of co-pyrolysis oil were found by Juan D Martínez et al. (2014) while investigating co-pyrolysis of forestry waste with ST.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

- Liquid yield increased with increase in addition of ST in SCB and was maximum for SCB/ST 3:1
- Overall carbon content of the SCB/ST 3:1 oil was higher and oxygen content was much lower than that of pure SCB oil and was comparable to pure ST oil
- Considering calorific value, viscosity, composition and other characteristics of the co-pyrolysis oil it can be concluded that co-pyrolysis process significantly improved the fuel characteristics of the product oil as compared to that of pure SCB oil
- Hence, there is a possibility of using co-pyrolysis oil as feedstock for fuel preparation.

5.2 Recommendation

- To perform co-pyrolysis studies using different biomass and Polyethylene
- Chemical and Thermal pretreatment of raw material before co-pyrolysis experiments
- Evaluate co-pyrolysis products using other blend ratios
- To analyse physico-chemical properties of char and gas for cost benefit analysis
- To perform experiments at high heating rate as high heating rate enhance liquid yield production

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