

Co-Pyrolysis of Wheat Straw and Waste Tires in Fixed-Bed Reactor



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Abstract

This study investigates the impact of addition of waste tire (WT) to wheat straw (WS) pyrolysis feedstock on consequent liquid yield quality and quantity. Samples of WS, WT and different blend ratios of the two wastes were fed to a fixed bed reactor. Reactor temperature was increased at 20°C/min up to 500°C as suggested by the thermogravimetric analysis of the feedstock. Nitrogen was used as sweeping gas. WS/WT 2:3 produced maximum liquid yield and its organic phase along with pyrolysis oils of WS and WT were further analyzed by GC-MS, FTIR, elemental analyzer and calorific value besides other physico-chemical properties. Addition of WT increased the calorific value (from 23.3 to 40.7 MJ/kg), carbon (58 to 85%) and hydrogen (8.6 to 9.6%) content and decreased oxygen content (from 32.8 to 5.1%) of the co-pyrolysis oil as compared to that of WS. Co-pyrolysis oil was also found to be more stable with significantly lesser proportion of aldehydes. Addition of WT to WS pyrolysis feedstock decreased the further fuel processing requirements to convert liquid yield into usable fuel, thus proved the co-pyrolysis as more favorable option for the management of the two waste types.

INTRODUCTION

1.1 Background

Rapid consumption of fossil fuel reserves has motivated the scientific society to discover alternate renewable energy resources. By 2042, coal reserve are estimated to be only fossil fuel remaining in the world which will last till 2112 (Shafiee et al., 2009). In last three decades, more than 50% of global research aimed to investigate alternate energy resources focused on biomass (Manzano-Agugliaro et al., 2013). With approximately 220 billion dry tons of biomass available each year globally, it is world's largest potential sustainable energy resource (Abnisa et al., 2014; Moreira, 2006). Wheat straw (WS) is considered as the second largest biomass type, next to rice straw (Kim et al., 2004). The wheat crop fulfills 21% of world's food demand and its requirement is increasing with growing population (Ortiz et al., 2008). Wheat is most widely grown crop in the world and is cultivated in over 115 countries. In 2008, global wheat production was estimated to be more than 650 teragram (Tg) (Atwell, 2001). Consequently, the global wheat residue production is approximately 850 Tg as ratio of residue/crop is estimated to be 1.3 on average. Although WS is partially used as animal feed, its extensive production creates problem for collection and disposal (Biswas et al., 2017). Throughout the history, burning of WS has been a common practice (Kerstetter et al., 2001) which has been creating problems like emissions of PM₁₀, CO and NO₂, adversely affecting human health, climate as well as environment (Talebnia et al., 2010; Yin et al., 2013). Hence it is critical to discover alternative options for safe WS disposal. On the other hand, Lopez et al. (2017) reported an estimated 1.4 billion tires being manufactured worldwide annually. With a proportion of waste tires (WT) being reused for various applications, large amount (800 million) still needs final disposal with a 2% annual increase (Huang et al., 2009). The accidental fire in WT storage are significantly frequent which cause emission of toxic compounds to the atmosphere (Juan Daniel Martínez et al., 2013). Hence, it is important to find out alternative routes for the utilization of WT in order to dispose it off in environmental friendly manner.

Pyrolysis has many environmental and technical advantages on other waste valorization processes. The significant one is the potential of liquid fuel production which can be easily stored and transported (Juan D Martínez et al., 2014). Numerous studies have been reported assessing the potential of bio-oil production from biomass via pyrolysis (A. V. Bridgwater, 2012; Czernik et al., 2004; Mohan et al., 2006; Oasmaa et al., 1999). The pyrolysis of biomass has attracted the scientific society to produce biofuels as it is renewable and alternative source for energy production. Several biomasses types such as WS (Mulligan et al., 2009), bagasse (Asadullah et al., 2007), and cotton stalk (Zheng et al., 2008) have been probed to be used as pyrolysis feedstock. Similarly in last two decades, the liquid fuel production from WT pyrolysis has also been investigated in multiple studies (Aylón et al., 2010; Juan Daniel Martínez et al., 2013; Oyedun et al., 2012; Taylor et al., 2013; Williams, 2013). Use of bio-oil is more environmental friendly as compared to fossil fuel as CO₂ emitted during combustion of aforementioned is the same which is consumed in photosynthesis while biomass is synthesized in the field (Vitolo et al., 1999). However, there are some drawbacks of bio-oil such as it contains higher oxygen content (around 45-50%) (Bridgwater, 2004), has lower volatility and calorific value as compared to those of more refined fossil fuels and has delayed ignition time (Cao et al., 2009). The low combustion efficiency in bio-oil is mainly because of the presence of oxygenated compounds. which also gives its molecule higher polarity, making it immiscible with petroleum fuel (Lu et al., 2009). Hence, for improving the bio-oil quality, upgrading processes such as hydrodeoxygenation and catalytic cracking are commonly in practice (Mortensen et al., 2011). The high cost of solvents, catalysts and large quantity of hydrogen involved in upgradation processes marginalize the economic feasibility of bio-oil (Zhang et al., 2013). So, there is a need to establish innovative technique for making pyrolysis bio-oil a practical alternate fuel.

1.2 Problem statement

As stated previously, it is important to discover new technique for production of upgraded liquid oil, it is also significant to find out new biomass source as a feedstock for pyrolysis process which has potential to be used in as source of energy. Globally, biomass sources are different in each country, so this issue has prime importance to investigate availability of biomass as alternative

source of energy. The wheat crop is cultivated in large areas of Pakistan and the surplus amount of wheat residue (wheat straw) is considered as waste. The proper handling of wheat straw (WS) needs extra attention. The literature survey shows that the unsatisfactory handling practices creates problems and have negative effects on environment. Consequently, its utilization should be for more valuable process such as in form of liquid fuel via pyrolysis process.

Furthermore, biomass pyrolysis oil has some draw backs in term of low calorific value (due to high amount of oxygen) Corrosiveness and instability. For improving the bio-oil quality, upgrading processes such as hydrodeoxygenation and catalytic cracking are commonly in practice. The high cost of solvents, catalysts, hydrogen-donors and complicated equipment used in these processes cost more than oil price. So, to reduce this cost a new approach is needed.

In terms of simplicity in design and effectiveness one technique shows potential for producing upgraded bio-oil from biomass. Moreover, the addition of any catalysts and hydrogen is not needed in this process. The technique is named as co-pyrolysis. The two or more feedstocks are used in this process. The normal pyrolysis and co-pyrolysis have almost same mechanisms. Many studies have been conducted on co-pyrolysis and reported that the liquid oil quality and quantity was improved after biomass co-pyrolysis. Therefore, to understand the process mechanism of co-pyrolysis this technique should be studied in detail.

1.3 Objectives of Study

- To maximize the bio-oil yield by adding waste tires in wheat straw in co-pyrolysis.
- To enhance the quality of bio-oil in co-pyrolysis with addition of waste tires.

LITERATURE REVIEW

2.1 Introduction

The reduction in fossil fuel resources such as petroleum, natural gas and coal has encouraged scientific society for the development of new approaches to invent or find renewable fuel. According to an article the availability of coal reserves will be till 2112 and after 2042 it will be the only fossil fuel available in the world (Shafiee & Topal, 2009). The environmental-friendly and high efficiency technologies are underway for development of alternative energy resources. For this purpose, the most of research was conducted for production of energy from biomass. In last three decades, the 56% of global research was done for production of renewable energy from biomass, 26% from solar energy, 11% from wind power, 5% from geothermal energy and 2% was done in hydropower (Manzano-Agugliaro et al., 2013). The biomasses are the world's largest available sustainable energy resources which can be utilize for most of research to produce energy from biomass and about 220 billion dry ton of biomasses are available in the world (Moreira, 2006)

The environmental concerns are also important for renewable energy besides the reduction of fossil fuels. In last decade, mainly after the earth summit '92, globally the environmental concerns about its danger and reality has been increased drastically (Agarwal, 2007). The primary pollutants emissions (carbon monoxide, oxides of nitrogen, sulfur dioxide and hydrocarbons) have increased the environmental problems such as ozone layer depletion, climate change globally and acid rain. Their production is mainly from combustion of fossil fuels (Kalogirou, 2004). The controlling of pollutant emission is necessary for reducing the environmental concerns. The usage of renewable energy resources the with in optimum ranges can provide option to reduce the negative effects on environment, also suppress the requirement for fossil fuels usage and can creates employment opportunities with increase the chances of export market (Manzano-Agugliaro et al., 2013).

For the substitute of fossil fuels a several number of alternative resources for energy are widely available in the world. It is vital to keep some factors in mind before selection of alternative source

of energy such as, proper availability of source, environmental and economic advantages. For this respect, biomass is the best source that has potential to address these challenges. So, the availability of biomass is very easy in many forms like, residue from wood and agriculture, crops which cultivated especially for energy and the solid waste generated from household (Easterly et al., 1996). The biomass energy and its contribution to economic growth was studied in emerging and 10 selected developing countries by (Bildirici, 2013). It was concluded that the energy from biomass is impetus for economic growth and it can reduce the poverty level of developing countries. This is because it always meets the energy requirements for all countries and there is no need of expensive devices for energy conversion. Still, the environmental benefits of biomass utilization for energy sources has been proven (Ahtikoski et al., 2008).

Biomass has been widely acknowledged for having potential as energy source and as a renewable energy it is only source which can be converted in many form as fuel like liquid, gas and char, which also gives flexibility in its production as a fuel and marketing. pyrolysis is such a process which always recommended to accomplish this goal. T. Bridgwater (2006) has reported that currently this process has gained much consideration because it has ability to produce liquid oil in high yield around 70% with provision of optimum conditions like final temperature around 500°C and 1 second residence time for hot vapors. However, after adjusting the operating parameters the other products (gas and char) yield can also be optimized. The liquid obtained from pyrolysis is known as bio-oil or pyrolysis oil, which has ability to utilize as fuel or in many commodity chemicals as a feedstock. A. Bridgwater et al. (1999), reported that the oil has potential to be directly used in many applications like, furnaces, boilers, diesel engines and also in turbines for production of electricity without any upgrading processes. The main advantage of pyrolysis oil with respect to environment is that the emission of greenhouse gases is lower as compared to fossil fuel (Vitolo et al., 1999).

Regardless, the pyrolysis oil is environmental friendly but it has low characteristics as compared to fossil fuel, specifically the combustion efficiency. The low combustion efficiency in bio-oil is mainly because of the presence of oxygenated compounds. The pyrolysis oil from biomass contains high amount of oxygen (35-60 wt.%) (Bridgwater et al., 1999; Guillain et al., 2009; Oasmaa & Czernik, 1999; Parihar et al., 2007). In more than 200 different compounds the oxygen can be identified which mostly found in form of water (Oasmaa & Czernik, 1999). The low

calorific value, instability of oil and corrosion problems is because of these oxygenated compounds (Lu et al., 2009).

For solving the challenges in bio-oil applications it is vital to improve its quality and the main important is elimination of oxygen content. The bio-oil upgradation techniques have been applied in many studies. The hydrodeoxygenation (HDO) and catalytic cracking are most commonly practiced to achieve this goal. The catalytic cracking is further divided into offline and online catalytic cracking. In offline technique, the liquid oil is used as a raw material and in online technique the vapors produced during pyrolysis are used as a raw material (Hew et al., 2010). This method is proved to be low cost than HDO but results of this process are not seemed to be good because 8-25% coke is produced in during this process and poor fuel quality is obtained. Furthermore, Scheirs (2006) reported that the catalyst addition during pyrolysis process creates some problem:

- Due to catalyst consuming during process the running cost increase;
- The poisoning/deactivation of catalyst after some time reduce its life cycle;
- The solid residue increased in the presence of catalyst which also increase the disposal cost.

Moreover, the low-grade bio-oil converting into hydrocarbons the HDO is a suitable process (Toba et al., 2011). The amount of hydrocarbon is increased in fuel after HDO process that's why this process received more attention (Joshi et al., 2012). The use of complicated equipment, high pressure requirement during reaction and addition of catalyst increase the cost and complexity of process. So, innovative technique is needed to reduce the process cost with improved bio-oil quality.

2.2 Importance of co-pyrolysis process

The important factors in developing a new technique for production of better quality liquid oil are simplicity and the effectiveness. In this respect, biomass co-pyrolysis technique has potential to meet these criteria. The two or more different feedstocks are used in co-pyrolysis process. Many studies have been conducted on co-pyrolysis and reported that the liquid oil quality and quantity was improved after biomass co-pyrolysis and this technique does not require any upgradation in

the system. The better performance/cost ratio of co-pyrolysis shows a potential to be used in industrial applications as compared to catalytic cracking and HDO.

The synergistic effect is the main successful key of co-pyrolysis process that occurs during different material interaction during this process. The Panda et al. (2010), studied the plastic and woody biomass co-pyrolysis and concluded that the enhancement in liquid oil yield was obtained after incorporation of plastic and calorific value of oil was also higher than bio-oil from woody biomass alone that was due to hydrocarbon polymers containing olefins, paraffins, aromatics, naphthenes and higher calorific value of non-condensable gases.

The blending of bio-oil from biomass and liquid oil from waste tires or plastic looks impossible and operational cost may be increased. The polar nature of bio-oil from biomass is responsible for making it immiscible with liquid oil from waste tires or plastic. The mixing of these oil together form an unstable mixture which cause breakage of phase separation after short period. The separate pyrolysis of biomass and waste tires or plastic requires more energy and production of oil cost will rise significantly. So, due to the problems associated with blending of oil the co-pyrolysis process found to be optimal technique for production of homogenous oil. The co-pyrolysis process forms the stable oil due to interaction of radicals.

Furthermore, during the co-pyrolysis process the reduction in volume of waste material occurs more significantly because more feedstock is consumed. This process has additional benefits like, to reduce the need for landfill, waste treatment cost can be saved and resolving a lot of environmental issues. The method of landfilling for waste disposal is objectionable (Garforth et al., 2004), the waste reduction as well as enhancement in energy security can be achieved by co-pyrolysis because it is substitute for management of waste. Regarding economic perspective, biomass conversion to oil from co-pyrolysis is considered as promising option. Kuppens et al. (2010) , studied the synergetic effects occurs during flash co-pyrolysis and its economic significance. They reported that biomass co-pyrolysis seems to be more profitable technique than simple pyrolysis process and it can also increase the economic development.

2.3 Co-pyrolysis mechanism

The pyrolysis and co-pyrolysis both have nearly same mechanism. Basically, the experiment is performed in the absence of oxygen in a closed apparatus with moderate temperature. To produce oil from co-pyrolysis process three step are required,

- Sample preparation
- Co-pyrolysis experiment
- Condensation of vapors to be converted into liquid oil

The steps in co-pyrolysis process of biomass for producing oil are given in **Figure 2.1**. The drying and crushing of sample should be achieved before co-pyrolysis. The oven drying (at 105°C for 24 hours) can be used for drying of raw material. The heat requirement for pyrolysis process and in additional intermediate processes (drying of biomass) can be fulfilled by combustion of byproducts from pyrolysis process (char and gas) (Veses et al., 2014). The aim of biomass drying is to remove the moisture content from sample. The high amount of moisture in raw material leads to increase the water content in oil. So, the moisture content in the sample should not be more than 10% (A. V. Bridgwater, 2012).

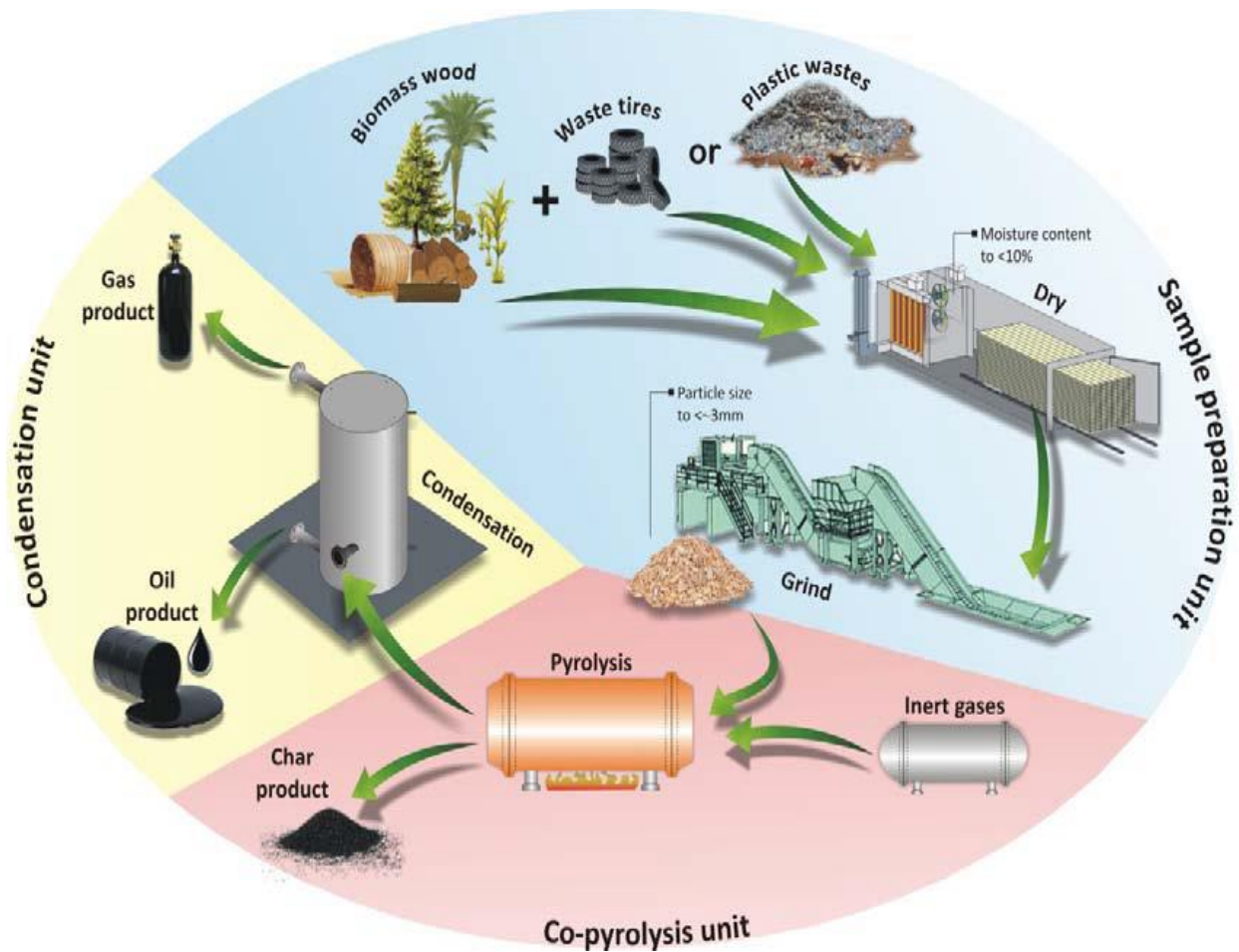


Figure 2.1: Co-pyrolysis process of biomass

In co-pyrolysis, inert gas is used as a sweeping gas to accelerate the hot vapors in pyrolysis zone to the condenser (cooling zone). To avoid the secondary reactions during process and to enhance the liquid oil yield less than 2seconds residence time of hot vapor is required (A. V. Bridgwater, 2012). Nitrogen (N₂) is a cheaper gas than other gases and it is inert in nature, so in pyrolysis and co-pyrolysis N₂ gas is commonly used. Several studies investigated the influence of inert gas on pyrolysis yield and reported that it has potential to effect on liquid oil yield (Abnisa et al., 2011). The optimum flow rate of inert gas can increase the pyrolysis oil yield, whereas reduction in oil yield can be observed at high flow rates. Although, its flow rate varies with the type of reactor. Moreover, there is several parameters which influenced the pyrolysis process such as, biomass type, heating rate, final temperature and raw material particle size. Akhtar et al. (2012),

comprehensive reviewed the influence of different parameters on optimum bio-oil yield from biomass pyrolysis. In co-pyrolysis experiment, generally the temperature between 400-600°C should be adjusted for production of maximum oil. This temperature range can produced above 45% liquid oil. However, after identification of raw material characteristics optimum temperature is adjusted for producing maximum liquid oil. Consequently, for determination of raw material characteristics thermogravimetric analysis (TGA) should be performed.

Another important step in pyrolysis and co-pyrolysis is condensation for producing liquid oil. This step is significant because without condensation only gas and char can be produced. When hot vapors pass through condensation unit their gaseous state change into liquid phase. By introducing the inert gas in the reactor, the residence time of vapors is controlled. To obtain the high pyrolysis oil yield fast condensation of vapors is required. The reduction in molecular weight of liquid oil has been observed at lower temperature (<400°C) of vapors. Because secondary condensation reaction occurs at low temperature. So, the vapors temperature should be >400°C before entering the condensation unit to reduce the deposition of liquid as well as blockage in piping and equipment should be avoided (A. Bridgwater et al., 1999).

The feedstock ratio is a special parameter used in co-pyrolysis in contrast to pyrolysis process. In requirement for extra oil production this parameter has much importance. Sharypov et al. (2002), co-pyrolyzed the synthetic polymer and wood biomass mixture and concluded that feedstock (biomass/plastic) ratio has significance in term of liquid oil production. The (Abnisa et al., 2013), reported the similar tendency in co-pyrolysis study that in three main parameters (feedstock ratio, reaction time and temperature), feedstock ratio was the most important variable which affected the liquid oil yield.

2.4 Feedstock and co-pyrolysis process

Several resources for renewable energy are available in the world such as, biomass energy, solar energy, wind energy and geothermal energy. Among all, only biomass can produce fuel in liquid, char and gas form in pyrolysis process. Although the biomass pyrolysis fuel has low calorific value as compared to fossil fuel, the co-pyrolysis process can improve the oil quality. In current section, feedstock selection and availability was discussed which has potential to be used in co-pyrolysis.

2.4.1 Feedstock selection

Some type of biomass can be used in co-pyrolysis for enhancement in oil quantity and quality. In this respect, it is important to study for selection of proper biomass wastes. Recently, in many co-pyrolysis studies many types of biomass (wood and agriculture residue, dedicated energy crops and municipal solid wastes) were investigated and showed promising results. Different types of biomass used in co-pyrolysis are given in **Table 2.1**.

Table 2.1: Different types of biomass used in co-pyrolysis

Biomass type	Biomass
Agriculture residue	oat straw, wheat straw (Ateş, 2011), sugarcane bagasse (García-Pérez et al., 2002), corn stalk (Cordella et al., 2013), rice husk (Ye et al., 2008).
Wood residue	pine wood (Sharypov et al., 2002), Beech wood (Sharypov et al., 2002)
Municipal solid wastes (with industrial wastes)	Polystyrene (Abnisa et al., 2013), wheat straw (Samanya et al., 2012), electronic and electrical waste (Liu et al., 2013), Palm shell (Abnisa et al., 2013). potato skin (Önal et al., 2012).
Crops especially dedicated for energy	Switch grass (Weiland et al., 2012), Rapeseed (Samanya et al., 2012), willow (Cornelissen et al., 2008a), sorghum (Cordella et al., 2013).

The elemental composition (Carbon, Hydrogen, Oxygen, Nitrogen and sulfur) and physical properties like calorific value, moisture content, ash content of different biomass are given in **Table 2.2**.

Table 2.2: Properties of different biomass.

Biomass type	C (wt.%)	H (wt.%)	O (wt.%)	N (wt.%)	S (wt.%)	Ash (wt.%)	Moisture (wt.%)	HHV (MJ/Kg)
wheat straw	38.34	5.47	55.22	0.6	0.37	6.63	12.81	14.68
Rapeseed	58.81	8.57	23.46	3.67	-	5.78	5.15	26.70 ^a
Rice husks	48.36	5.13	32.79	0.72	0.31	12.5	6.8	16.79
Mixed wood	47.58	5.87	42.1	0.2	0.03	2.1	7.76	-
Rice straw	36.89	5	37.89	0.4	-	19.8	-	16.73
Pine wood	45.92	5.27	48.24	0.22	-	0.35	7.99	18.98 ^b
Almond shell	47.63	5.71	44.48	-	-	2.18	-	-
Coconut shell	47.97	5.88	45.57	0.3	-	0.5	-	19.45
Walnut shell	50.48	6.41	41.21	0.39	-	1.4	8.11	19.2a

a Assumed higher heating value (HHV) for dry basis

b Dry ash-free basis

In general, three components are present in biomass like, hemicellulose, cellulose and lignin (Hamelinck et al., 2005; Hames et al., 2003). Biomass main constituent's hemicellulose and cellulose degradation occurred temperature of 200-260°C and 240-350°C respectively. The molecular weight of lignin is high and its degradation occurred at 350-650°C (Mohan et al., 2006; Bridgwater et al., 1999). The components of different biomass in weight (wt.) percent are given in **Table 2.3**.

Table 2.3: The components of different biomass

Components	Oreganum stalk	Wheat straw	Poplar aspen	Corn cob	Corn stover
Cellulose (wt.%)	33.8	32.4	42.3	31.7	31.0
Hemicellulose (wt.%)	9.3	41.8	31.0	3.4	43.0
Lignin (wt.%)	10.9	16.7	16.2	31.7	13.0

In tire manufacturing process, 60-65% rubber, 25-35% carbon black and the rest consisting of fillers and accelerators are added in tire. The different types of natural and synthetic rubbers are added such as, polyisoprene (natural rubber), chloroprene, styrene butadiene, nitrile and polybutadiene rubber. Generally, the natural rubber originated from Hevea tree and the petroleum based precursors (monomers) polymerization form synthetic rubber tree (Martínez et al., 2013). Depending on different parameters, the tire pyrolysis can produce liquid oil, gas and char yield of 25-75%, 5-57% and 26-49 % by weight respectively. The liquid oil from tire pyrolysis has high calorific value around 44MJ/kg. it contains mostly aromatic and aliphatic compounds, lower oxygen content and has high H/C ratio around 1.5 (Martínez et al., 2013).

Table 2.4: The production of Tires in different countries for period of 2006-2007.

Countries	Yearly production (thousands of units)	
	2006	2007
China	274,230	336,700
U.S	200,281	195,000
Japan	175,916	176,207
South Korea	81,508	85,853
Germany	75,342	75,218
France	59,000	61,300
Brazil	42,216	not available
Indonesia	41,300	44,300
Russia	40,417	42,330
India	32,880	33,695
Canada	30,216	33,303
Italy	32,017	31,140
Poland	28,931	30,747
Thailand	26,931	not available
Turkey	23,905	25,795
Romania	14,761	16,600
Malaysia	11,560	13,420

Petroleum is a limited and esteemed natural resource and its most quantity (above 70%) is consumed in transportation (Ghosh & Prelas, 2009). It is considered as end product and due to its extensive usage in transportation may result in its shortage. However, in tire and plastic some part of it is still stored in different forms. Management of these wastes needs extra attention because these wastes have important properties to be used as fuel. The utilization of these wastes in co-pyrolysis process can produce improved liquid oil.

2.4.2 Feedstock availability

Before selection of feedstock as alternative source of energy it is important to consider its availability. In this regard, biomass mass is in sufficient quantity to meet this criterion. The total accumulation of biomass waste is high as it is generated from many sources such as forestry, industries, sewage, agriculture activities, municipal solid waste, animals and from food processing activities. The type of biomass is always different for each country depending upon several factors like lifestyle, population, geographical conditions, agriculture development, industrial growth, economic growth, forest development, and food demand. This means that for production of liquid oil from biomass co-pyrolysis each country has same opportunity.

Williams et al. (2013) reported an estimation that globally production of tires is 1.5 billion which will become waste after their consumption. The production of Tires in different countries for period of 2006-2007 is given in **Table 2.4**. The increase in waste tires proportion has severe impact on urban waste stream and it's a big threat for environment. Quek & Balasubramanian et al. (2013) reported that major proportion of waste tires (approximately 64%) is illegally dumped or landfilled or stockpiled and their recycling amount is only 13%. The degradation of waste tires is not easy, so in landfill facility due to trapped gases waste tires tend to float on top after some time resulted in breakage of landfill covers. The emissions of toxic (mutagenic and carcinogenic chemicals) gases is occurred due to incineration of waste tires. The waste tires are needed special treatment for their disposal. For this purpose, pyrolysis is a feasible option for treatment of this waste and recovery of valuable products.

The waste tires have high calorific value as compared to biomass that why their utilization in co-pyrolysis as co-feed is useful source for production of liquid oil. Their availability is in massive amounts and are particularly easier to find in almost all countries. The proper usage of waste tires in co-pyrolysis will be a new innovative concept for enhancement of energy security, environmental concerns and waste management. So, application of co-pyrolysis process for liquid oil production will be favorable in all countries.

2.5 Reactor types for pyrolysis

During pyrolysis experiments role of reactor type is important for attaining desire distribution of product. There are different types of reactors which include fluidized bed reactor, circulating bed reactor and fixed bed reactor.

2.5.1 Fluidized bed reactor

In fluidized bed reactor, different phase of chemical reactions can be achieved. The fluid material in this reactor (liquid or gas) is passed at very high velocity through granular solid which can suspend the solid.

2.5.2 Fixed Bed Reactor

In fixed bed reactor, feedstock material is fed in powder or in form of pellets which is packed in static bed. The sweeping gas (N_2) is introduced in the bed and reaction between feedstocks is induced when temperature of reactor is raised. The nitrogen gas is passed because it is non-reactive gas and helps in carrying hot mixture of gases out of the reactor. The hot mixture of gases condensed in condensers and change into liquid oil.

2.5.3 Circulating bed reactor

The feedstocks are introduced at very fine particle size in fluidized bed reactor in order to fluidize these fine particles rather at high velocity of gas, are to blown out from bed and reactor, and replaced with fresh solids. So these are called circulating beds.

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.

2.6 Co-pyrolysis studies exploration

It is important to explore the co-pyrolysis studies in order to make concept about production of high quality pyrolysis liquid oil. For this purpose, researchers have made many efforts to understand this technique and have reported interesting findings.

2.6.1 Use of waste tires in co-pyrolysis

The researchers have growing interest for using waste tires (as a fuel source) in pyrolysis process. Several comprehensive reviews have been published for liquid fuel production through pyrolysis of waste tires (Martínez et al., 2013; Quek & Balasubramanian, 2013; Williams, 2013). Several studies for co-pyrolysis of waste tires with other materials are summarized in **Table 2.5**. There was no involvement of solvents, catalysts and pressure in studies which are summarized in **Table 2.5**.

Table 2.5: Several studies of the use of waste tires in co-pyrolysis

References	Description of material	Reactor configuration and operating conditions	Results and observations
(Cao et al., 2009)	Particle size: Waste tire = < 165 μ m Sawdust = 198-360 μ m Tire/sawdust ratios: 0:100, 40:60, 60:40, 100	Reactor: Fixed bed reactor Sample size: 100g Heating rate: 20°C/min Final temperature: 500°C and hold 3.5 hours	The liquid oil yield was increased from 45% to 46.2, 47 and 47.2% when waste tires were added 0%, 40, 60 and 100% by mass respectively. The caloric value of sawdust was 28.52MJ/kg and raised to 42.44MJ/kg when waste tires were 60% by mass.

References	Description of material	Reactor configuration and operating conditions	Results and observations
(Alias et al., 2011)	The empty fruit bunches (EFB) were co-pyrolyzed with waste tires (without wire steel).	Reactor: Fixed bed reactor Sweeping gas: nitrogen Final temperature: 500°C Ice/water condenser: for collection of pyrolysis oil.	Co-Pyrolysis products: Liquid: 42.80% Char: 33.20% Gas: 24% The liquid oil quantity was reduced in pyrolysis of EFB alone.
(Siva et al., 2013)	Particle size: Scrap tire (ST) = < 2 mm Bilge water oil (BW) and oily sludge (OS) were mixed with ST. ST/BW and ST/OS ratios: 1:1 and 1:1.	Reactor: Fixed bed reactor made of stainless steel (length: 210mm and diameter: 60mm) under atmospheric pressure. Final temperature: 500°C	The increase in oil yield was observed from 44.1% (in pyrolysis of ST alone) to 64.8, 62.4 in co-pyrolysis of ST/BW and ST/OS and caloric value was increased from 43.8, 44.8 and 44.9MJ/kg respectively.

References	Description of material	Reactor configuration and operating conditions	Results and observations
(Martinez et al., 2014)	Particle size: Pinewood chips (PWC) = 15mm Waste tire = 5mm	Reactor: Fixed bed reactor (length: 74cm and internal diameter: 1.6cm) and auger reactor (mass flow rate: 5kg/h) Heating rate: 80°C/min Final temperature: 500°C PWC and Tire %: 100% biomass, 90%, 80% and 100 waste tires	In fixed bed reactor, the 50% and 47.6% oil yield was obtained for PWC and waste tire alone respectively and no increase in liquid oil yield was observed with addition of waste tire. In auger reactor, the PWC yield was 52% and with addition of 10% waste tire yield was increased to 56%. So, the auger reactor yield higher than fixed bed reactor. Author also reported that with addition of waste tire the calorific value was improved than calorific value of biomass alone

2.7 Economic feasibility assessment

Due to simplicity during design and in operation, the co-pyrolysis process has produced upgraded fuel and enhanced the yield. So, use of this technique can perform important role for development of biomass energy industry. From an economic point of view. An important note showed the feasibility of co-pyrolysis.

Kuppens et al. (2010) used the net present value (NPV) to evaluate the economics of flash co-pyrolysis of 1:1 w/w ratio blends of biomass (willow) and biopolymers (PLA, corn starch, PHB, bioppearls, eastar, solanyl, and potato starch). NPV is the best analysis method for selecting or rejecting an investment, either industrial or financial (Graham & Harvey, 2001; Pasqual et al., 2013; Vanreppelen et al., 2011). The rule in this analysis was that the project would be accepted if the NPV was greater than or equal to zero, and would be rejected when the NPV was less than zero (Aziz, 2013). In this regard, the study performed by Kuppens et al. showed that flash co-pyrolysis of willow with any biopolymer was economically more interesting than flash pyrolysis of pure willow, because the NPV of co-pyrolysis resulted in positive cash flows for all types of biopolymers used. This result is supported by some other estimations as well, including the initial investment expenditure, the production costs, and the possible revenues. The author also noted that the calculations in this research paper were from a case study in Belgium, but the economic model behind the case study can be adapted to other locations.

In addition, an economic evaluation of the co-pyrolysis process was also studied by Shelley and El-Halwagi (1999). A techno-economic feasibility study was performed to assess the viability of co-liquefying scrap tires and plastic waste into liquid transportation fuels. The return on investment (ROI) approach was used to make investment decisions; if the ROI was positive then the investment was considered profitable. The authors noted that the co-liquefaction of waste plastic and scrap tires as well as the liquefaction of scrap tires alone was both technically and economically feasible. The results showed promising economics for the mixed materials case with an ROI of approximately 18%, as compared to only 12% for the plastics alone scenario. The author also reported that the tipping fees obtained for the raw materials used in the process were the key to overall profitability. Similarly, it is in agreement with another study performed in 1998 by Huffman and Shah (1998), who reported that the ROI depends on the tipping fees received for waste plastics and tires. The high tipping fees received will be linearly contributed to the increase in ROI.

2.8 Discussion on co-pyrolysis scenarios

This review showed that many researchers have studied the potency of co-pyrolysis technique using various types of biomass wastes like, oat straw, wheat straw (Ateş, 2011), sugarcane bagasse (García-Pérez et al., 2002), corn stalk (Cordella et al., 2013), rice husk (Ye et al., 2008), 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.

MATERIALS AND METHODS

3.1 Raw materials

The samples of WS used for experiments were taken from a farm in Rawalpindi, Pakistan. It was ground and sieved to obtain particle size of 0.6-1.8mm. The WT sample was taken from Taxila, Pakistan. Textile netting and steel cords were already removed from WT by the vendor. Same particle size as WS, was achieved by grinding and sieving. The raw material processing is given in **Figure 3.1**.

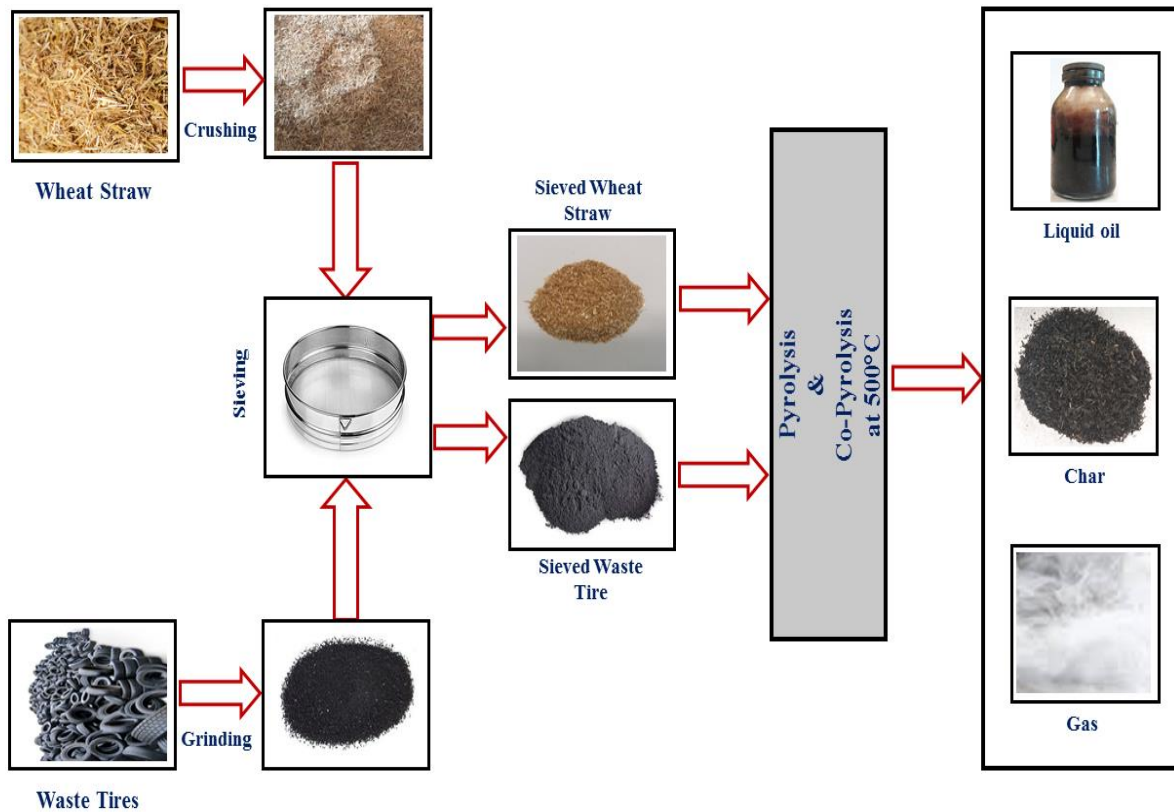


Figure 3.1: The raw material processing

3.2 Experimental setup and pyrolysis procedure

The components of experimental setup are given in **Figure 3.2**. The experimental setup contains,

1. Fixed bed reactor
2. Ceramic resistance furnace
3. Two condensers
4. PID temperature controller
5. Flow meter for Nitrogen
6. Arduino circuit
7. Thermocouple



Figure 3.2 : Components of experimental setup

The pyrolysis and co-pyrolysis of WS and WT was performed in fixed bed reactor, made of stainless steel, having length of 50.8cm and internal diameter of 10.8cm as shown in **Figure 3.3**. For each batch run, 200g of sample was fed into the reactor. The blend ratios of WS and WT used in the experiments were 1:0, 4:1, 3:2, 2:3 and 0:1. Three repetitions of each blend ratio were carried out to ensure reproducibility of results. The heating rate of reactor was set to 20°C/min from ambient to 500°C and kept constant there for 30 minutes. N₂ gas was introduced at the rate of 50ml/min from bottom of reactor as sweeping gas. N₂ flow was maintained before start of heating process to purge the air from reactor. Vapors and gases produced during pyrolysis and co-pyrolysis process were removed from top of the reactor along with N₂. Hot mixture of gases was passed through two condensers in a series with first condenser having tap water at 20-25°C on cooling

side and second condenser having iced water (mixed with NaCl) at -2 to -5°C. The conical flasks fitted to condensers collected the produced oil.

Once the run was completed, quantities of liquid and char obtained were weighed separately and amount of gas produced was calculated from difference of initial sample weight and collective weight of liquid and char produced. The liquid products obtained from pyrolysis and co-pyrolysis contained organic phase (OP) and aqueous phase (AP). Pyrolysis oil of WT and co-pyrolysis oils were separated by separating funnel as after four hour retention, AP and OP formed separate layers. In case of WS oil however, AP and OP did not form separate layer even after four hour retention. The two phases were separated after addition of diethyl ether. OP was filtered by filtration assembly using anhydrous sodium sulfate bed. The process has already been reported in literature (Uçar et al., 2014). Only OP was considered for further analysis.

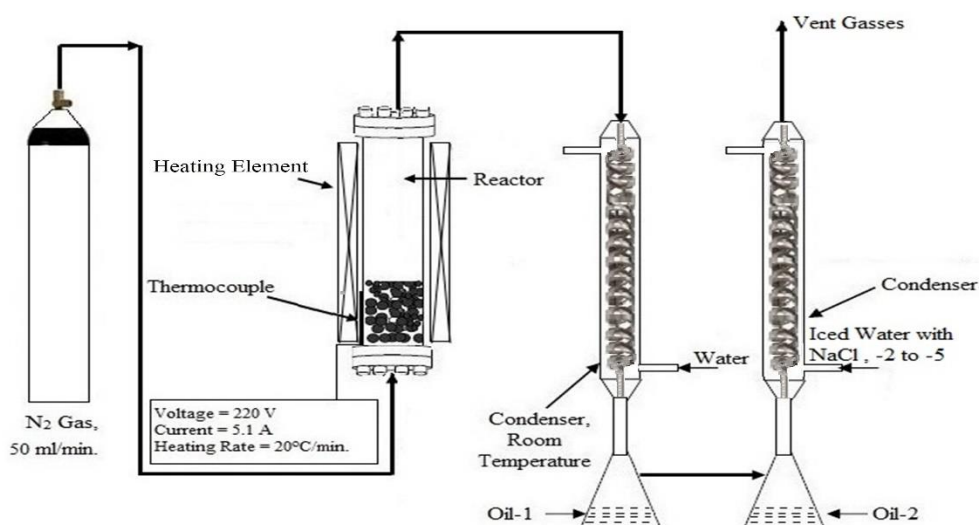


Figure 3.3: Schematic diagram of pyrolysis reactor

3.3 Raw material and product characterization

3.3.1 Raw material analysis

Thermogravimetric (TG) Analysis of raw samples of WS and WT was performed in Mettler Toledo for determination of thermal behavior of feedstock during pyrolysis. Nitrogen gas was used for keeping the atmosphere inert and the experiments were performed at heating rate of 20°C/min. The raw samples were tested following ASTM D3172-07 for proximate analysis and ASTM D7291-96 (LECO CHNS-932) for elemental composition. The calorific values of the feedstock were determined with LECO AC-500 Isoperibol Calorimeter (ASTM D240) and component analysis was determined by following previously reported method (Yang et al., 2006).

3.3.2 Liquid product analysis

Physico-chemical properties of liquid yield samples of WS, WT and selected blend were determined by different ASTM methods. The ASTM D5373 (LECO CHNS-932 analyzer) was applied for determination of elemental composition whereas the specific gravity and kinematic viscosities were measured according to ASTM D4052-96 and ASTM D445 respectively. Calorific value of the oil samples was measured by LECO AC-500 Isoperibol Calorimeter (ASTM D240), flash point by Setaflash series 3 (ASTM D7236) and pH was determined using Hach Sension 156 Multimeter.

Major compounds in the WS, WT and selected WS/WT oil samples were identified by GC-MS (Shimadzu QP2020). The column used was SH-Rxi-5sil Ms capillary column with a length of 30m, diameter of 0.5mm and having film thickness of 0.5µm. The experiment started at 40°C and the temperature was held there for 5 minutes. Then temperature was raised to 175°C at heating rate of 3°C/min and was held there for 5 minutes. The temperature was further increased to 200°C at heating rate of 5°C/min followed by a hold for 5 minutes. In the end temperature was raised from 200-250°C at a heating rate of 5°C/min and held there for 5 minutes.

The functional group analysis of WS, WT and selected WS/WT blend oils was performed by using FTIR (Bruker Spectrum 400 spectrometer). The samples were scanned in the range of 550–4000cm⁻¹ with a resolution of 2cm⁻¹.

RESULTS AND DISCUSSION

4.1 Feedstock analysis

The results of proximate and elemental analysis, calorific value, and component analysis of WS and WT are given in **Table 4 1**.

Table 4.1: Properties of WS and WT.

Feed	WS	WT
Proximate Analysis (Weight%)		
Moisture	9.66	1.85
Volatile Matter	68.34	66.73
Fixed Carbon	15.2	28.20
Ash	6.8	3.22
Elemental Analysis (Weight%)		
Carbon	45.79	85.06
Hydrogen	5.71	7.56
Nitrogen	0.73	0.63
Oxygen + Sulfur	47.77	6.75
Lignocellulosic Composition (Weight%)		
Extractives	8.5	–
Hemicellulose	38.3	–
Lignin	20.7	–
Cellulose	32.5	–
Calorific Value (MJ/kg)	16.97	37.63

The proximate analysis results showed that the volatile matter was the largest constituent of both WS and WT. Omar et al. (2011) reported that high reactivity and volatility of pyrolysis oil can be achieved by high volatile content in the feedstock which also increases the liquid yield. In contrast, higher ash content will reduce the liquid product. The results of elemental analysis showed that WT has lower amount of oxygen and higher amount of hydrogen as compared to WS. Hence it is expected that the calorific value of liquid oil will improve with addition of WT in pyrolysis of WS.

The TG curves of WS and WT are given in **Figure 4.1**. First weight loss in WS sample occurred near 100°C which is associated with evaporation of water. The hemicellulose thermal decomposition started at 250°C and the cellulose content started to degrade at 300°C. The lignin decomposition was in wide range between 200-500°C. The combined thermal decomposition of cellulose, hemicellulose and lignin occurred between 250-450°C (Mulligan et al., 2009). The decomposition of WT started at 300°C and occurred in two steps. In first step, natural rubber got decomposed followed by decomposition of butadiene and styrene butadiene rubber mixture in the second step. Significant mass of WT decomposed between 300-500°C which was in line with previous reports (Uçar & Karagöz, 2014). Both, previously published literature and TGA results obtained in this study showed that significant weight loss of WS and WT samples occurred till 500°C and beyond this temperature, the weight loss was comparatively low. Hence final temperature of the pyrolysis process was selected to be 500°C.

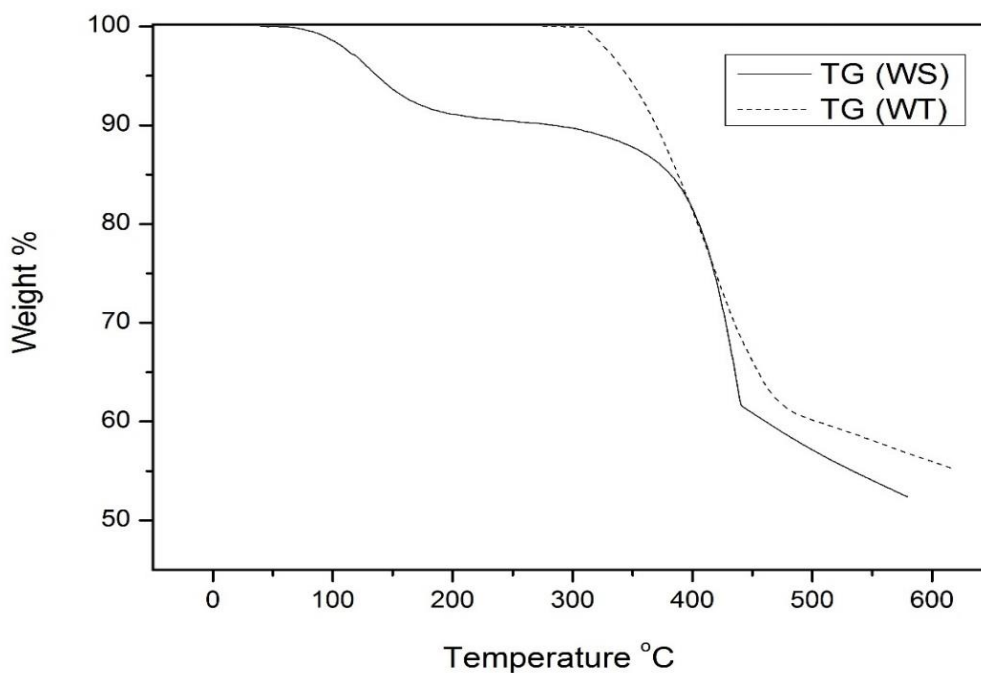


Figure 4.1: TG curves of WS and WT.

4.2 The product yield

The distribution of products obtained from WS and WT pyrolysis and co-pyrolysis at different blend ratios are given in **Figure 4.2**. The liquid yield obtained was higher than char and gas yield for both pyrolysis and all combinations of co-pyrolysis. There was significant increase in liquid yield after addition of WT in WS for co-pyrolysis experiments. The liquid yield increased from 35 % (WS pyrolysis) to 37.5%, 39.8%, and 41.5% and 44% when WT addition was 20%, 40%, 60% and 100% by mass respectively. The increase in liquid yield with addition of WT was also observed in previous studies (Cao et al., 2009). This increase is attributed to higher amount of hydrocarbons provided by WT in co-pyrolysis. Similarly, the char production also increased (from 31.8% to 32.6%, 34.7%, 35.9%, and 37.6%) with increased proportion of WT in the feedstock. In a similar study, Abnisa et al. (2015) have explained that higher percentage of fixed carbon in WT is mainly responsible for increment of char in co-pyrolysis experiments, as carbon black is added

during manufacturing of tires. Reduction in gas yield (from 33.2% to 29.9, 25.5, 22.6 and 18.4%) was observed after addition of WT. Since WS/WT 2:3 produced maximum liquid yield, the co-pyrolysis oil of this blend ratio along with pyrolysis oils of WS and WT were further characterized in this study for comparison.

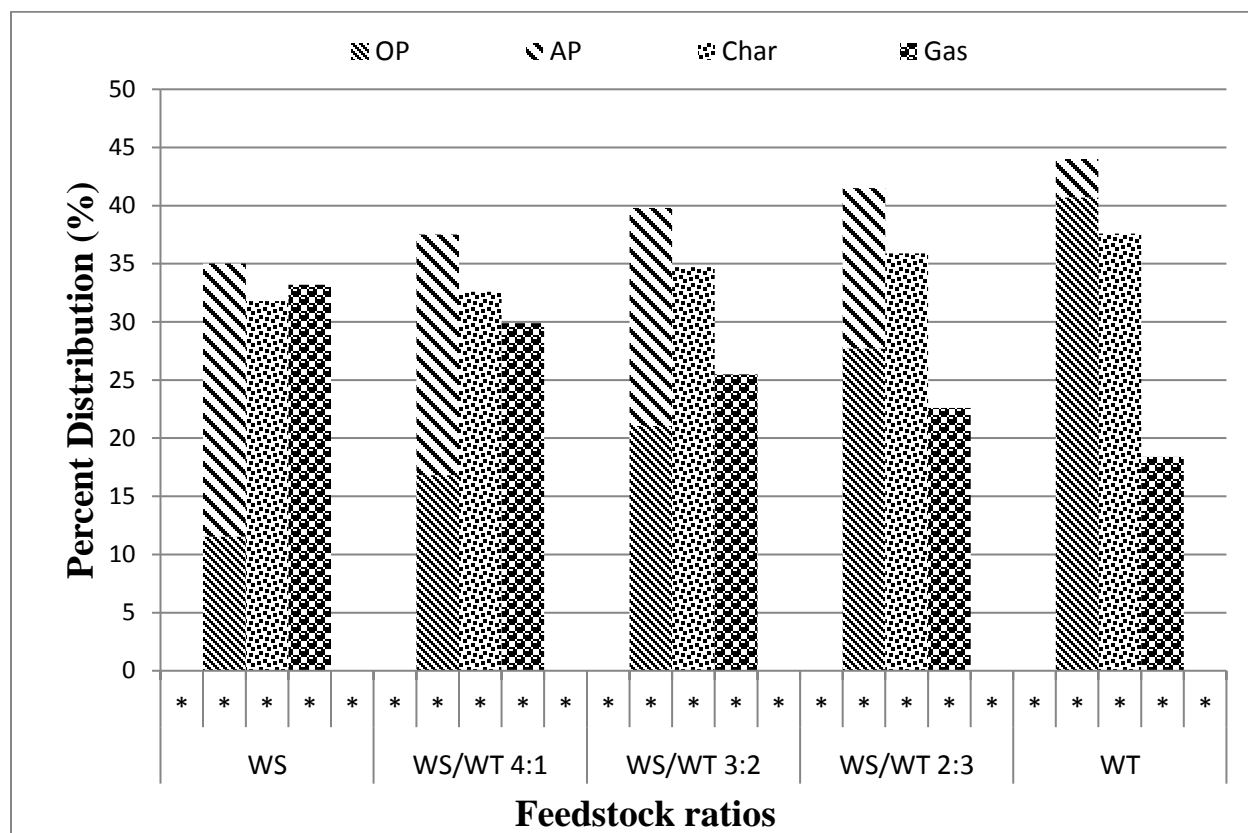


Figure 4.2: Distribution of products obtained from pyrolysis and co-pyrolysis.

4.3 Liquid product characterization

The physico-chemical properties of the pyrolysis and co-pyrolysis (WS/WT 2:3) oils are given in **Figure 4.3 (a, b, c, d, e, f)**. The calorific value and carbon content was found to be increased and oxygen content decreased in WS/WT 2:3 oil as compared to WS oil. Hence it can be concluded that addition of WT has significantly enhanced the quality of WS pyrolysis oil.

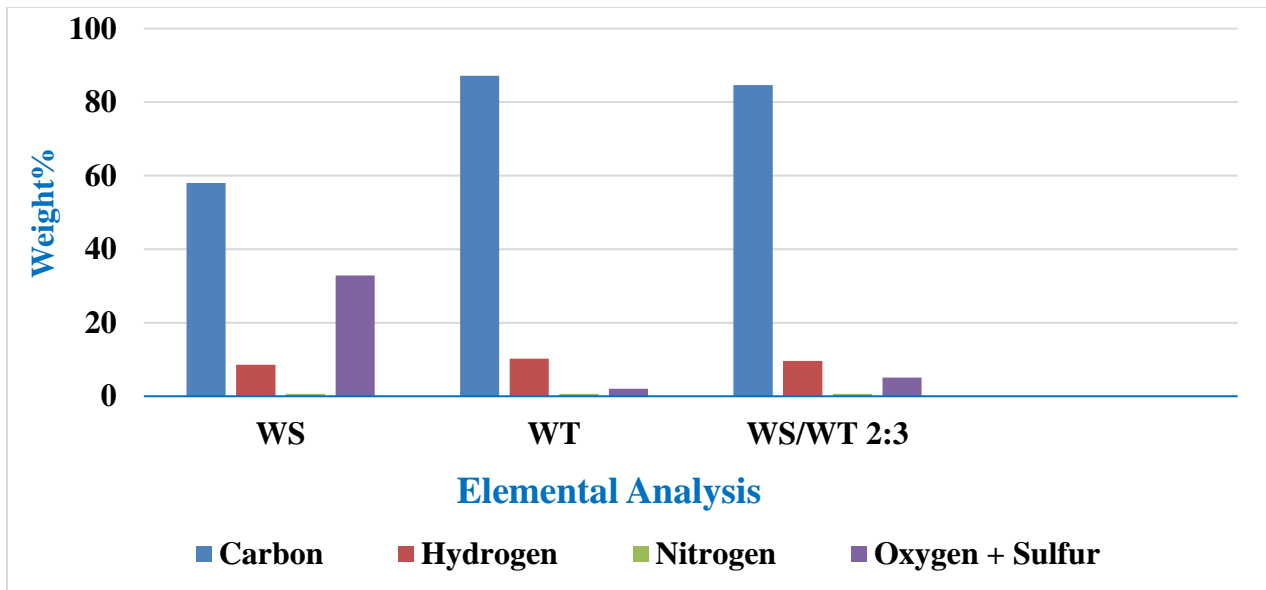


Figure 4.3 (a): Elemental properties of oils.

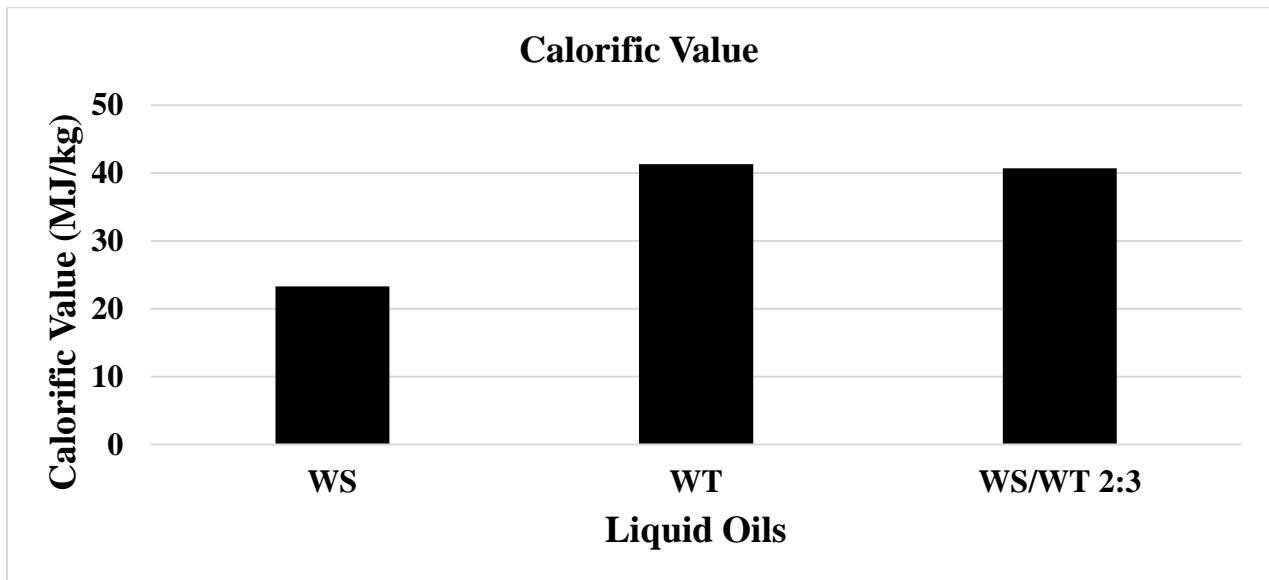


Figure 4.3 (b): Calorific values of oils.

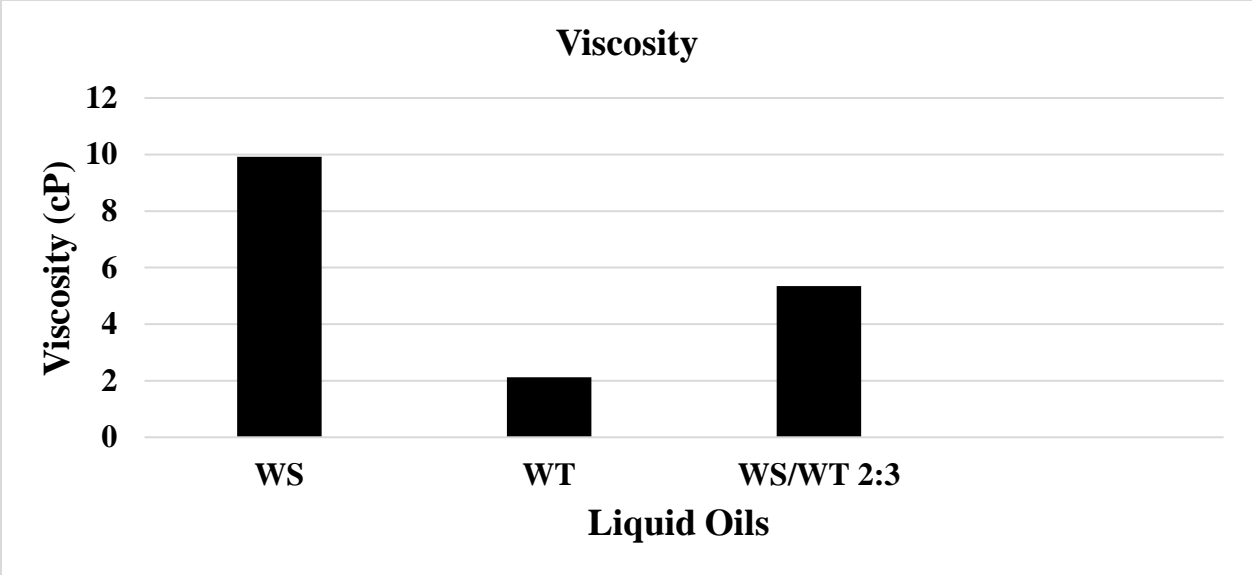


Figure 4.3 (c): Viscosities of oils.

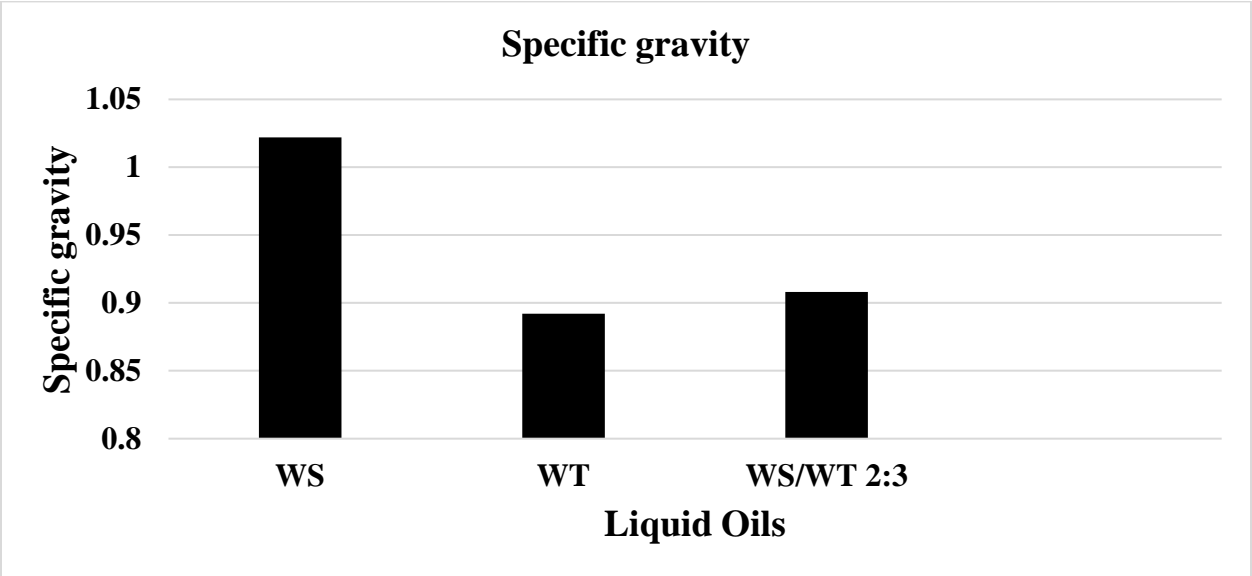


Figure 4.3 (d): Specific gravity of oils.

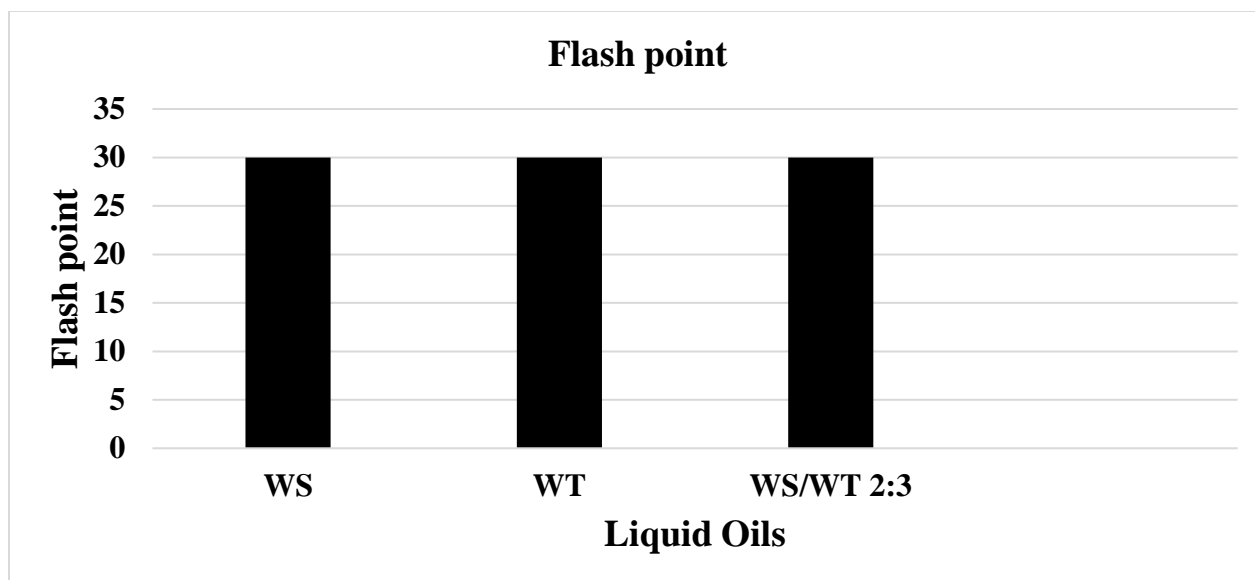


Figure 4.3 (e): Flash point of oils.

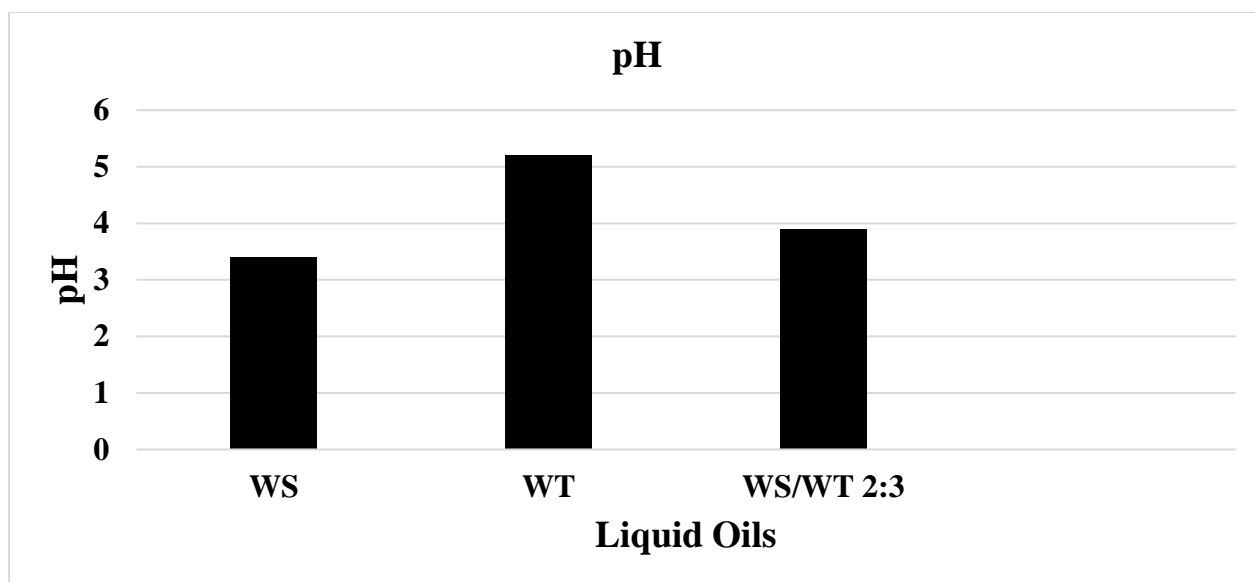


Figure 4.3 (f): pH of oils.

The major compounds identified in GC-MS analysis of the oil samples are listed in **Table 4.2** for comparison. The phenol derivatives compounds were mainly identified in WS oil which are attributed to be formed by the decomposition of lignin present in biomass (Lu et al., 2009; Mohan et al., 2006; Ortiz et al., 2008). Phenol and 2-methylphenol were major compounds present in WS

oil. The WT-derived oil was mainly composed of methylbenzene, 1,4-dimethylbenzene and D-limonene. The previous studies involving WT pyrolysis have explained that thermal decomposition of natural rubber (polyisoprene) promotes the formation of limonene in high quantity (Mastral et al., 2000; Pakdel et al., 2001) which also explains the presence of significant amount of D-limonene in WS/WT 2:3 oil. However, WS/WT 2:3 oil also acquired some compounds such as 2-methylphenol and 4-ethylphenol from the thermal decomposition of WS content in the blend. The composition of WS/WT 2:3 oil showed higher similarity with WT oil as compared to that of WS. Most of phenolic, aldehydes and ketonic compounds identified in WS pyrolysis bio-oil were not detected in WS/WT 2:3 oil. The reduction in aldehydes is important for the stability of the oil as presence of aldehydes is reported to decrease the oil stability (Djokic et al., 2012). Juan D Martínez et al. (2014), reported similar decrease in phenolic, aldehydes and ketonic compounds with the addition of WT in biomass pyrolysis. One downside of the WS/WT 2:3 oil appeared in GC-MS analysis was presence of significant amounts of PAHs which are considered to be carcinogenic (Sánchez et al., 2009) and thus environmentally unfavorable. PAHs were undetectable in WS oil and much lower in WT oil which attribute their formation due to synergistic effect of co-pyrolysis. One possible route for PAHs formation is Diels–Alder reaction in which pyrolysis of alkanes produces alkene and dienes and upon cyclization, they consequently form PAHs (Cypres, 1987; Fairburn et al., 1990). Intermediate alkane formation in WS/WT 2:3 oil was confirmed by FTIR analysis presented later in this study, which makes Diels-Alder reaction to be more probable route of PAHs formation. Besides, previous studies (Cypres, 1987; Egsgaard et al., 2001) have also reported PAHs formation by the secondary reactions of phenols deoxygenation.

Table 4.2: Major compounds identified in GC-MS analysis of oil.

S.No.	R.T. (min)	Name of Compounds	% Area		
			WS	WT	WS/WT 2:3
Benzene derivatives					
1	3.75	Methylbenzene	2.62	12.49	5.98
2	7.01	Ethylbenzene		2.78	1.79
3	7.4	1,4-Dimethylbenzene		11.52	13.44
4	12.17	1-ethyl-2-methyl-Benzene		2.5	5.96
5	12.85	1,2,3-trimethyl-Benzene		9.11	5.04
6	13.86	alpha.-Methylstyrene		1.14	
7	16.01	1,2-propadienyl-Benzene		2.33	
8	20.14	2,4-Dimethylstyrene		2.22	
9	21.41	1-methyl-1,2-propadienyl-Benzene		2.77	
10	26.46	2-cyclopropylethenyl-Benzene		1.08	
Phenols					
11	13.06	Phenol	9.27		1.85
12	17.39	2-Methylphenol	7.89		0.83
13	18.31	2-Methoxyphenol	7.76		
14	20.85	4-ethyl-2-methoxy-phenol	0.76		
15	21.98	2,5-Dimethylphenol	1.77		
16	22.44	4-Ethylphenol	1.5		1.02
17	22.86	2,6-dimethoxyPhenol	2.57		
18	23.47	2-Methoxy-5-Methylphenol	0.72		
19	23.81	1,2-Benzenediol	4.38		
20	24.99	Benzothiazole		1.48	1.16
21	26.75	3-Methyl-1,2-Benzenediol	3.09		
Terpenes					
22	13.73	D-Limonene		17.07	14.04

S.No.	R.T. (min)	Name of Compounds	% Area		
			WS	WT	WS/WT 2:3
Olefins					
23	3.44	3-methyl-2,4-Hexadiene		1.07	
24	4.11	1,3,6-Heptatriene		0.91	
25	4.45	(E)-3-Undecene		0.8	
26	5.57	1,2-dimethyl-Cyclohexene		1.08	
27	5.95	4-ethenyl-Cyclohexene		2.64	1
28	8.42	1-ethynyl-1-Cyclohexene		5.19	
29	12.73	7,7-dimethyl-1,3,5-Cycloheptatriene		1.16	
30	15.22	1-Isopropenyl-4-methyl-1,3-cyclohexadiene		3.57	
31	16.82	3-bromo-1,5-Cyclooctadiene		0.89	
32	16.92	3,7,7-trimethyl-1,3,5-Cycloheptatriene		0.76	
33	17.95	3-ethylidene-2-methyl-1-Hexen-4-yne		1	
34	18.61	3-methylene-4-(1,2-propadienyl)-Cyclohexene		1.32	
Alkanes					
35	3.84	Methylene-Cyclohexane		0.97	
36	45.23	Heptadecane			3.23
Aldehydes and ketones					
37	2.17	1-hydroxy, 2-propanone		1.63	
38	3.22	1-methyl-3-Cyclohexen-1-ol			0.56
39	5.89	Furfural		5.08	

S.No.	R.T. (min)	Name of Compounds	% Area		
			WS	WT	WS/WT 2:3
40	6.86	2-Furanmethanol		4.42	
41	7.63	1-(Acetyloxy)-2-propanone		2.55	
42	9.21	2-methyl-2-Cyclopenten-1-one		2.03	
43	10.96	3-methyl-2-Cyclopenten-1-one		1.81	
44	11.96	5-Methylfurfural		1.15	
45	12.96	3-methyl-1,2-Cyclopentanedione		3.19	
46	13.01	cis-1,2-Dihydrocatechol			1.24
47	15.81	2,3-dimethyl-2-Cyclopenten-1-one		1.42	
48	16.04	3-ethyl-2-hydroxy-2-Cyclopenten-1-one		1.13	
49	20.75	Hydroquinone		1.3	
50	24.12	4-Hydroxy-3-methoxybenzaldehyde		0.84	
Polycyclic aromatic hydrocarbon (PAH)					
51	23.01	Naphthalene			5.62
52	28.27	1,4-dihydro-1,4-Methanonaphthalene			1.7
53	28.61	1-Methyl-Naphthalene			10.5
54	33.46	2,3-dimethyl-Naphthalene			2.94

S.No.	R.T. (min)	Name of Compounds	% Area		
			WS	WT	WS/WT 2:3
55	34.63	1-(2-methylphenyliminomethyl)- Naphthalene-2-ol			1.64
56	38.52	1,2-dihydro-6-methyl-Naphthalene			0.5
Acids and acid derivatives					
57	2.42	Propanoic acid		2.78	
58	4.23	Butanoic acid		0.73	
59	4.75	2-Nonynoic acid			1.27
60	12.96	3-(2-carboxycyclohexanoylamino)- Benzoic acid			1.03

The FTIR spectra of WS, WT and WS/WT 2:3 oils are given in **Figure 4.4**. The wave number ranges representing different functional groups are given in **Table 4.3**. The FTIR results show that the WS/WT 2:3 oil, had much lower phenols and alcohol content as compared to WS oil. According to Juan D Martínez et al. (2014), the decomposition of lignin (present in biomass) enhances the formation of phenols and alcohols. The C-H stretching and bending is due to the presence of alkanes. The increase in peaks for C-H stretching was observed in WS/WT 2:3 as compared to WS oil as well as WT oil. Although, C-H bending can be seen in all WS, WT and WS/WT 2:3 oils, it is more prominent in WS/WT 2:3 oil which can be attributed to the synergistic effect in co-pyrolysis process. The similar results for alkanes have been reported in literature while investigating the co-pyrolysis of WT and palm shell (Abnisa & Daud, 2015). The ketones, aldehydes and carboxylic acids were observed in WS oil because of presence of high oxygen content and their peaks were reduced in WT and WS/WT 2:3 oils. These results are also confirmed by the ultimate analysis of the three oil samples which show a reduction of, oxygen content from 32.6% in WS to 4.6% in WS/WT 2:3 oil.

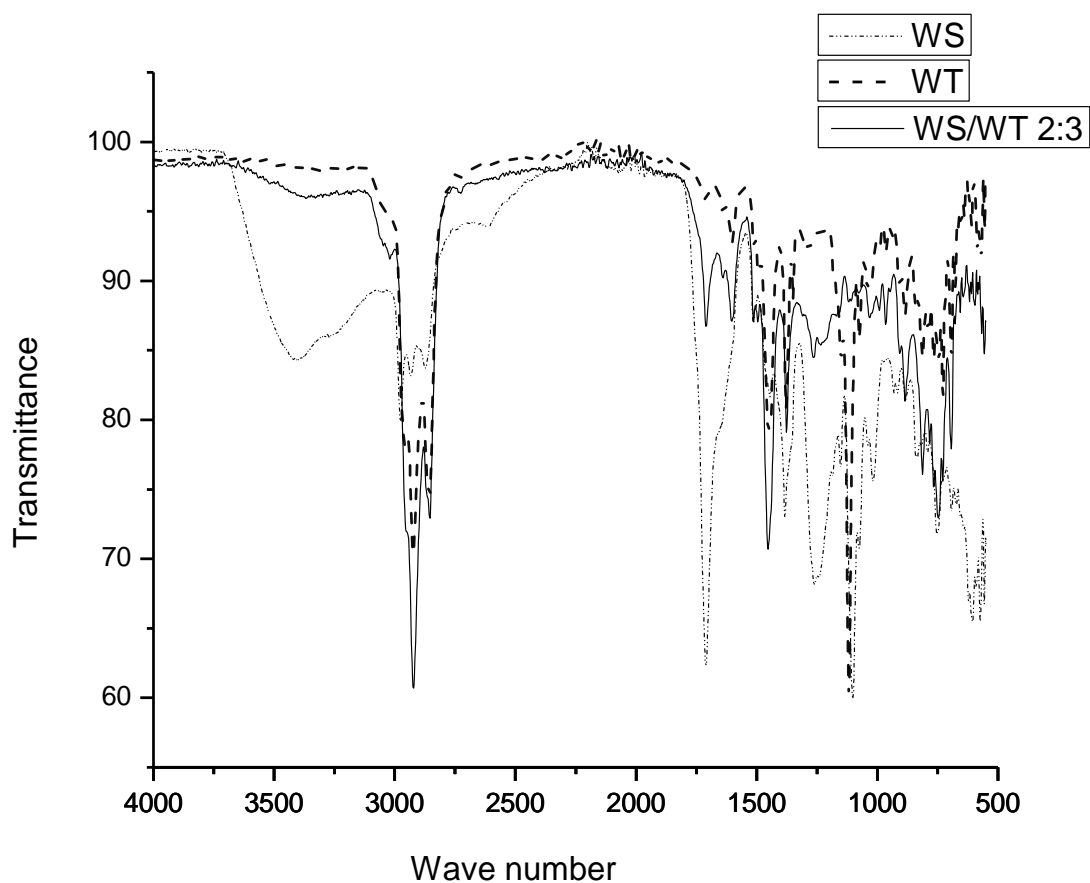


Figure 4.4: FTIR spectra of OP from WS, WT and WS/WT 2:3.

Table 4.3: The ranges of different functional groups with respect to wave number.

Type of Functional Group	Wave number, (cm-1)	Class of Compound	WS	WT	WS/WT 2:3
O–H stretching	3,600–3,200	Phenols, alcohols	✓	✓	✓
C–H stretching	3,000–2,850	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	✓	✓	✓

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Effect of waste tire (WT) addition on the oil yield quantity and quality of wheat straw (WS) pyrolysis was investigated in this study. Liquid yield as well as organic phase increased with addition of WT. Calorific value and carbon and hydrogen contents of the co-pyrolysis oil increased whereas oxygen content and viscosity decreased, showing upgraded oil quality as compared to that of WS. GC-MS results of co-pyrolysis oil showed reduced amounts of aldehydes, phenolic and ketonic compounds thus indicated its higher stability. However, increased proportion of PAH in oil was a downside of co-pyrolysis. Keeping quality parameters in view, it is concluded that co-pyrolysis oil can be considered to be used as feedstock for fuel preparation after lesser further processing as compared to that of WS oil, thus giving better option for management of wastes like WS and WT.

5.2 Recommendations

- The Vacuum and pressurized co-pyrolysis of WS and WT can also be studied to analyze its effect on yield and quality improvement.
- The high heating rate for raw material heating during co-pyrolysis can enhance the oil yield.
- The analysis of Char & Gas can be performed for their further utilization.

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