Enhancing aromatics in oil yield of waste tire and rice straw co-pyrolysis using dual catalytic bed of HZSM-5 and metal oxides (CaO/MgO)

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Certificate

It is certified that the contents and form of the thesis entitled

“*Enhancing aromatics in oil yield of waste tire and rice straw co-pyrolysis using dual catalytic bed of HZSM-5 and metal oxides (CaO/MgO***)**”

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I certify that this research work titled "*Enhancing aromatics in oil yield of waste tire and rice straw co-pyrolysis using dual catalytic bed of HZSM-5 and metal oxides (CaO/MgO)*" 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

Catalytic co-pyrolysis of waste tire (WT) and rice straw (RS) was carried out in the fixed bed reactor. The effect of acidic HZSM-5, basic oxides (CaO/MgO) and their combinations on the quantity and quality of liquid oil was investigated. Relative Yield of aromatic hydrocarbons increased in the presence of catalysts while the oxygenates and other unwanted products decreased. Results revealed that dual catalytic bed of HZSM-5: MgO optimal ratio of 1:3 produced higher amounts of Mono-aromatic Hydrocarbons (48.7 wt%) and lesser unwanted Poly-aromatic Hydrocarbons (28.7 wt%). Selectivity of aromatics shows that combination of HZSM-5 with MgO was comparatively more effective than with CaO. Moreover, the application of dual catalytic bed significantly upgraded the physical characteristics and calorific value of pyrolytic oil was improved to 40.7 Mj/Kg which was comparable to the conventional fuels 43.1 Mj/Kg.

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List of Abbreviation

HC	Hydrocarbons
HHV	High Heating Value
LHV	Low heating value
PAH	Polycyclic Aromatic Hydrocarbon
MAH	Monocyclic Aromatic Hydrocarbon
AAE	Alkali and Alkaline earth metals
HDO	Hydro-deoxygenation
HY	Hierarchical zeolites
EHI	Effective hydrogen index
AC	Activated carbon
WT	Waste tire
RS	Rice Straw
SS	Stainless Steel
AP	Aqueous phase
OP	Organic phase
TGA	Thermogravimetric analysis
BET	Brunauer–Emmett–Teller
AL-SBA-15	Aluminum-substituted mesoporous material
ZSM-5	Zeolite Socony Mobil–5
MZSM-5	Micro/Meso porous ZSM-5
NR	Natural Rubber
SBR	Styrene Butadiene Rubber
BR	Butadiene Rubber

BJH	Barrett–Joyner–Halenda
DFT	Density functional theory
XRF	X-ray Fluorescence
F:C	Feedstock to Catalyst ratio

Introduction

1.1 Background

World economy is highly dependent on energy. Conventional fuels like petroleum, coal, and natural gas are significant contributors in global energy mix (Asadullah et al. 2007). The ever-rising worldwide energy demand is likely to deplete the nonrenewable fossil fuel reserves, causing the worldwide energy crises in the near future (Hassan, Lim, and Hameed 2019). Besides, extravagant consumption of fossil fuels has resulted in the increased production of harmful pollutants such as sulfur dioxide, nitrogen oxides and carbon dioxide, posing threats to the environment concerning greenhouse effect, global warming, and acid rain (Hassan et al. 2019). World needs environmentally safe and sustainable resources of energy as alternative to the fossil fuels (Hua and Li 2016). Waste has become a significant source of energy in the recent times. Two common categories of waste materials are fossil-based and bio-based wastes. Waste tires (WT) are the dominant of fossil-based waste, about 1.5billion tires being manufactured globally every year and disposed of in to the environment (Uçar and Karagöz 2014). Tires are composed of various materials including mainly vulcanized rubber, rubberized fabric, reinforcing textile cords, steel belts, and steel-wire reinforcing beads. Three types of rubbers are commonly used in the manufacturing of tires; natural rubber (NR), styrene butadiene rubber (SBR), and butadiene rubber (BR). Some additives are also added to enhance the performance of tires e.g. carbon black is added to give strength, extender oil (a mixture of aromatic HCs) softens the rubber and improves its workability (Sharma et al. 2000).

Globally, various types of biomass wastes are produced in significant amounts e.g. agricultural residues and forestry products having potential to be used as feedstock in energy production through different physio-chemical and biological processes including direct combustion, aerobic and anaerobic digestion, gasification and pyrolysis (Asadullah et al. 2007). The widely accepted stance of biomass as a green energy source is due to its abundance and property of carbon neutrality (Dai et al. 2017). Approximately 220 Billion dry tons of agricultural biomass is produced annually (Shah et al. 2019). Further, about 660 million tons of rice is produced all over the world every year, generating 800million tons of residue making RS and rice husk combined, as the most abundant agricultural residue available (Jin et al. 2019).

Pyrolysis is a thermal treatment process mainly focused on producing bio-oil from solid waste, while combustible gases can be produced via gasification (Asadullah et al. 2007). Biofuels possess various advantages over fossil fuels considering sustainability and less environmental impacts. Catalytic pyrolysis has been extensively investigated by the researches as a promising technique to produce biofuels from different wastes including biomass (Y. Wang et al. 2017).

The oil produced from biomass pyrolysis normally exhibits certain unwanted characteristics e.g. like high water and oxygen content causing low calorific value and combustion efficiency, higher aldehyde and ketone content (causing unstable nature), high viscosity, high volatility, and corrosiveness, restricting the direct usage of bio-oil as fuel. One potential option for upgrading bio-oil quality is the co-pyrolysis of biomass with polymers or WT as latter has higher H/C ratio and its presence in feedstock increases the overall hydrogen availability in pyrolysis reactions, converting the oxygenates into much wanted aromatic HCs (Uçar and Karagöz 2014). Positive synergistic effects have been observed in many studies of co-pyrolysis of WT with biomass (Cao et al. 2009; Martínez et al. 2014; Navarro et al. 2012). Furthermore, use of certain catalysts e.g.

zeolites, has been reported to improve the yield and quality of liquid oil obtained from co-pyrolysis of WT and biomass as it promotes selective reactions during pyrolysis process (Boxiong et al. 2007).

Various studies investigated the synergistic effect of acidic HZSM-5 with basic oxide catalysts on pyrolysis oil yield and composition noticeably enhanced yield of aromatics and little amount of alkylated phenols were observed by Fan et al. (2016) while investigating the catalytic co-pyrolysis of lignin and LDPE in the presence of HZSM-5 and MgO catalyst. Use of dual catalytic bed of HZSM-5 and CaO for co-pyrolysis of hemicellulose and plastics reported to cause increased yield of aromatics and other HCs like alkanes and alkenes (Ding et al. 2018). A similar study revealed that CaO-HZSM-5 dual catalyst use increased aromatic yield to about 35.8 wt%, surpassing the aromatic yield by 17 wt% with HZSM-5 alone (Liu et al. 2016).

MgO was used as catalyst to investigate its deoxygenation potential for bio-oil. Results showed that the basic sites of MgO helped to reduce acid formation and deoxygenation by promoting ketonization and aldolcondensation reactions. Oxygen was removed in the form of CO_2 (Stefanidis et al. 2016).

In this study the dual catalytic effect on WT-RS co-pyrolysis product yield and oil quality is investigated. Dual catalyst bed consisted of acid catalyst (HZSM-5) and two different basic catalysts (CaO/MgO). To the best of authors knowledge, the effect of this combination of catalysts on the co-pyrolysis of WT and RS has never been reported before. Varied ratios of catalysts HZSM-5 to CaO and HZSM-5 to MgO were applied in the co-pyrolysis experiments. The quality of obtained liquid oil was analyzed for chemical and physical characteristics by different analytical techniques including Gas Chromatography-Mass Spectrometry (GC-MS), calorimetry.

1.2 Problem Statement

Degradation of global fossil fuel reserves while world’s 80% energy requirements are being met conventional fuels, has directed the global research towards sustainable means of energy conversion (Gollakota et al., 2016). Under these circumstances pyrolysis of biomass as renewable energy source is highly recommended. In combination to waste-to-energy converter, pyrolysis can be used as feedstock recycling technique for HC waste such as wide variety of plastics and WT for cracking them into HC oil, gases and char (Chen et al., 2014).

However, direct application of bio-oil as fuel is limited because of high viscosity, water content, acidic nature, solid and ash content and its highly non-homogenous nature. Among several mechanisms that have been developed, co-pyrolysis and catalytic cracking together have shown to notably upgrade bio-oil composition. Catalytic co-pyrolysis has shown considerable synergistic effect in the product fractional yield, coke formation inhibition and increased fine-tune performance of catalyst.

Among the catalyst applied in pyrolysis, HZSM-5 has gained recognizable attention due to its special shape and structure selectivity, however being microporous (0.4-1nm), rapid deactivation and low HC yield has encouraged the use of mesoporous (2-50nm) catalyst with effective deoxygenation and deacidification ability, in combination to zeolite. The combined effect of acidic HZSM-5 and basic CaO and MgO on pyrolytic oil is analyzed in this study.

1.3 Objectives of the Study

- To investigate the potential and determine the optimal mass ratio of HZSM-5:CaO and HZSM-5:MgO for co-pyrolytic oil upgradation
- To analyze physicochemical characteristics of selected pyrolysis product oil

Literature Review

2.1 Pyrolysis

Pyrolysis is an endothermic process that thermally decomposes a material in the temperature varied from 300-1000°C in an inert environment without oxygen. This process is not only known to overcome increasing energy crises as it can derive energy from renewable resource like biomass, but is as well highly recommended technique for waste management (Abnisa et al., 2014), acting an effective waste-to-energy converter along with feedstock recycling technique. Pyrolysis yield three main products from waste material cracking i.e. bio-oil, char and gases (Lam et al., 2016). It is reported that lower temperature promotes char production, operating temperature of 500-550°C makes liquid yield as the major portion of products and further increase in temperature i.e. above 700°C syngas is the main product (Chen et al., 2015). However, depending on the feedstock and pyrolysis conditions, product composition and yield varies with oil (30–75 %), solid residues or char (10–35 %), and gas production (10–35 %) such as carbon monoxide, hydrogen, carbon dioxide and other light HCs (Kositkanawuth et al., 2014).

2.2 Pyrolysis products and applications

2.2.1 Oil

Pyrolysis oil which is the complex mixture of HC and oxygenated compounds is mostly referred to as bio-crude or bio-oil (Jahirul et al., 2014). Among the products of pyrolysis, oil is the most attractive one from an energy perspective as it can be used directly in many applications as liquid fuel for combustion in stationary low speed diesel engines (with high compression ratio) (Kositkanawuth et al., 2014), for small scale to large scale power generation in boilers, turbines and furnaces. Moreover, minimal greenhouse gas emissions make the oil product more environmental friendly fuel (Abnisa et al., 2014). Though bio-oil have 40-50% heating value of petroleum fuel, with less toxicity, enhanced lubricity and greater biodegradation property than HC fuel, it is still a preferable fuel (Gollakota et al. 2016).

2.2.2 Char

It is an amorphous rigid carbon matrix together with hydrogen and different inorganic species in two forms of crystalline graphene sheets or randomly ordered aromatic structure. Char physical properties are influenced by pyrolysis operating conditions, reactor type and feedstock used and its pre-treatment. However, varying chemical characteristics along with some physical properties are attributed by presence of heteroatoms hydrogen, nitrogen, oxygen and sulphur in the aromatic rings (Jahirul et al. 2014).

Bio-char can be used for soil amelioration; their application for improving crop yield has been well documented. Char is known to retain high levels of nutrients like K, P and Ca, so once added in soil under acidic conditions these nutrients are mobilized and easily up taken by plant roots. However, unlike organic compounds, heavy metals are not destroyed posing a toxic risk potential for agricultural application of char (Libra et al. 2011) .In many other industrial processes char can be used (Abnisa et al., 2014; Jahirul et al. 2014; Libra et al. 2011)

- As a solid fuel like in coal combustion or other waste, due to its low Sulphur content which makes it suitable for use in incineration
- Activated carbon (made by an activation step for increasing its sorption capacity) that can be used to adsorb heavy metal, organic dyes, arsenic compounds and many more organic and inorganic contaminants during water treatment.
- Carbon nanotubes and materials which possess high thermal stability can be used for catalyst support or as catalyst itself in liquid or gas phase
- CO_2 emissions can be controlled by utilizing CO_2 sorption ability of activated carbon and specific N-doped carbon materials at temperature of 150-500°C

2.2.3 Syngas

With increasing temperature, firstly the moisture present in feedstock evaporates which is then followed by primary reactions of thermal decomposition producing tar, charcoal and volatile compounds, which leave the biomass surface. Further cracking of tar and volatile compounds via secondary reactions of decarboxylation, deoxygenation, decarbonylation and dehydrogenation results in the formation of syngas comprising of H_2, CO and small amount of H_2O, CO_2, N_2 and other HCs. It is reported that HC cracking occurring at elevated temperature encourages H_2 formation, CO and CO_2 are produced from the decomposition of partially oxygenated organic species, and light HC generation from reformation of tar and high molecular weight HCs in the vapor phase (Jahirul et al. 2014).

H_2 to CO molar ratio in bio-gas influences its application in specific field, as higher H_2:CO appreciates the derivation of transportation fuel. Pyrolysis gas has a significant calorific value and thus can meet energy demand of pyrolysis process by its circulation back to the reactor, acting as a secondary heating source. Syngas could be recommended for use as an alternative fuel for internal combustion engines, owing to production of lower amount of unburnt HC and carbon monoxide in exhaust stream using pyrolysis gas (Abnisa et al. 2014; Jahirul et al. 2014; Kositkanawuth et al. 2014).

2.3 Classification of pyrolysis based on operating conditions

a) **Slow Pyrolysis**

b) **Intermediate Pyrolysis**

c) **Fast Pyrolysis**

d) **Flash Pyrolysis**

2.3.1 Intermediate Pyrolysis

It has operating conditions of somewhat in between slow and fast pyrolysis with 40-60% bio-oil yield. The products from it has exhibited to be more beneficial as unlike fast pyrolysis, it gives off oil that can be directly used as fuel due to presence of less reactive tar, along with dry char to be used in agricultural and energy application (Mohammed et al., 2016).

Table 2.1 Pyrolysis classification

Pyrolysis Type	Heat rate °C/sec	Temp °C	Particle Size mm	Vapor Residence time	Reference
Slow	0.1-1	400-600	5-50	5-30 mins or even 25-35h	(Demirbas, 2004; Dickerson et al., 2013; Singhania et al., 2018)
Intermediate		500-650		10-30sec	(Demirbas, 2004; Mohammed et al., 2016)
Fast	10-1000	850-1250	<1	0.5-2sec	(Demirbas, 2004; Singhania et al., 2018)
Flash	>1000	900-1200	<0.2	0.1-1sec	(Demirbas, 2004; Singhania et al., 2018)

2.4 Types of reactors

Different types of reactors have been employed in pyrolysis to optimize the waste-to-energy conversion process with high quality product oil.

a. **Batch and semi-batch reactor**
b. **Fixed Bed Reactor**
c. **Fluidized Bed Reactor**
d. **Ablative Reactor**
e. **Vacuum Reactor**
f. **Rotating Cone Reactor**
g. **Pyros Reactor**
h. **Auger Reactor**
i. **Plasma Reactor**
j. **Microwave Reactor**
k. **Solar Reactor**

2.4.1 Fixed Bed Reactor

In comparison to other reactors, fixed bed reactors are simple to design, construct and are easy to maintain and operate, making it cost-effective. A typical reactor is a steel, refractory brick or concrete structure with feeding unit, char removal outlet and a gas vent. These are best suitable for uniform sized feedstock with minimal composition of fine matter. Being operated at high solid residence time, less gas velocity and residue carry over, fixed bed reactors are applied for small scale energy production. Moreover, besides requiring specific feedstock size and its shape, such reactors with catalytic pyrolysis provides limited in-contact active site surface are for reactants (Al-Salem et al., 2017; Jahirul et al., 2014).

2.5 Operating Conditions

Pyrolysis reactions are affected by operating parameters of the process which not only changes the liquid yield but can improvise product quality with optimized conditions (Garba, 2017). Some of the important parameters are discussed below;

2.5.1 Temperature

Product distribution and composition varies remarkably with changing pyrolysis temperature. At temperature <300°C mainly heavy tar production occurs due to heteroatom site disruption in the biomass. Whereas at increasing temperature, various biomass bonds are broken down with increased endothermic reactions forming number of different compounds. Typically, in between 400-550°C oil production is maximum, however with further rise in temperature secondary degradation of vapors starts which promotes gas production (Akhtar et al., 2012).

2.5.2 Vapor residence time

It is one of the parameters that affect liquid-oil composition to greater extent than its yield (Jahirul et al., 2014). Generally, lower residence time of vapors increases oil production as flow of sweeping gas removes the vapors at higher rate from pyrolysis chamber inhibiting secondary reactions including re-polymerization, re-condensation and thermal cracking. Though less vapor residence time of about 1 second is needed for liquid yield, a study found that at keeping low pyrolysis temperature of 400°C residence time up to 5 seconds can give adequate quantity (Salehi et al., 2011).

2.5.3 Feed particle size

Optimized particle size for highest yield of products, depend on the type of feedstock added and the pyrolysis reactor employed. It has been observed that larger diameter of feedstock particle especially in conventional pyrolysis makes slow inter-particle heat transfer which enhances char production and limit oil yield. Whereas small particle size ranging 0.6 to 1.3 mm has shown to favor high volatile production due to uniform and rapid heat flow (Aysu et al. 2014).

2.5.4 Biomass heating rate

Higher rate of heating is preferred in pyrolysis as (Akhtar et al., 2012);

- It increases the degradation rate of biomass particles with fast depolymerization; tar is decomposed which leads to enhanced volatile yield
- Heat transfer limitations within the reactants is minimized, giving efficient

biomass conversion to liquefaction

- Improved bio-oil quality is obtained as it lessens the water content and oxygenated compounds in liquid yield
- Enhanced decarboxylation and decarbonylation gives abundance of CO_2 or CO in the gas composition

2.5.5 Sweeping gas

Different inert gases such as Nitrogen, Argon, hydrogen, steam are being used for removal of hot vapors from the system and therefore controls the vapor residence time. N_2 is most applied as it is cheaply available (Liu et al., 2014).

Typically, low gas velocity maximizes the liquid production, as increased flow rate of purging gas not only hinders the effective condensation of vapors but may also inhibit reactions which would have favored the oil production (Akhtar et al., 2012).

2.5.6 Retention time

It is widely accepted that shorter reaction time suppresses secondary reactions including tar and liquid oil compounds degradation to lighter compounds, which promotes the oil yield. Also giving less reaction time means per consumption of thermal unit, more will be the products formed which reduces the operating cost of the process, making it energy efficient.

Nevertheless, to ensure complete biomass conversion optimization of reaction time should be attained taking into account number of variables such as particle size, vapor residence time, reactor type and others (Akhtar et al., 2012; Xiu et al., 2010).

2.5.7 Initial pressure

In a study it has been observed that effect of operating pressure is correlated to temperature of the reactor i.e. higher the temperature greater the effect. One of the effects in products distribution is reported with lighter gaseous molecule production and decreased double bond products with elevated pressure (Al-Salem et al., 2017).

2.6 Type of feedstock

2.6.1 Biomass

As stated by US Energy Information Administration, 2009 almost 79% of total worlds demand of energy sector is fulfilled by fossil fuels (Gollakota et al., 2016). Being non-renewable and its depleting resources worldwide, fossil fuels replacement with biomass (where possible) as an energy source has drawn considerable attention. Several processes have been applied for waste to energy conversion, however pyrolysis has gained much attention with its ability to give the maximum liquid yield up to 75% wt (Abnisa et al., 2014).

Biomass used as feedstock is any substance that is composed of C, H, N, O and other inorganic elements, which come from mainly plants or animal waste. Three main components i.e. cellulose, hemicellulose and lignin, present in biomass contributes to its own decomposition time and behavior in pyrolysis.

Proximate analysis result of feedstock plays a crucial role in best feedstock selection. Generally, biomass with more volatile matter yields high amount of bio-oil and gas products, while high fixed carbon ratio promotes char production. Also presence of moisture in the feedstock influences the heat transfer activity which affects product distribution such as yielding higher amount of AP in liquid yield (Jahirul et al., 2014).

2.6.2 Fossil based waste

Fossil based wastes like plastics and WT can be used as a feedstock too by which it can be converted into valuable fuel and harmless disposable or landfill materials (Chen et al., 2015). WT are being generated at a higher rate due to the increasing production of vehicles. About 5.4 million tons of WTs are produced in China in 2010 (Hu et al. 2014), 3.3 million tons in Europe in 2007, 4.8 million tons in U.S., and 1.1 million tons in Japan (Elbaba, Wu, and Williams 2010).

They are the product of crude oil processing, and so possess high amount of hydrogen and carbon, encouraging its use as a higher value HC feedstock for pyrolysis.

2.7 Drawbacks of simple pyrolytic oil

Bio-oil derived from pyrolysis appears dark red-brown to dark green color, and the presence of lower molecular weight aldehydes and acids give it distinctive acrid smoky odor (Jahirul et al., 2014). Comparing with crude oil, bio-oil from pyrolysis has high-water content, density and significantly lower HHV, viscosity and PH. It is composed of several oxygenated compounds varying from low molecular weight like water (18 g/mol) to high molecular weight oligomers (up to 5000 g/mol). Water content of pyrolysis oil which is the result of dehydration reactions during the process and presence of initial moisture content in feedstock, leads to undesirable characteristics of fuel such as low energy density, reduced heating values, stability as well as non-homogenous nature and lowers the flame temperature which make ignition delay and decreased combustion rate compared to diesel fuels (Abnisa et al., 2014; Gollakota et al., 2016;

Yildiz et al., 2016). However to little benefit, presence of water is said to improve the flow characteristics i.e. reduces viscosity, lower NOx emissions and maintain uniform temperature inside the combustion chamber.

Along with water, presence of oxygenated compounds attributes to lower values of PH referring to high acidity, corrosiveness and non-volatility and aging during storage (Garba, 2017). Oil gets more viscous, volatile compounds are lost, tar deposition with time and phase separation occurrence is the result of physical and chemical changes in oil characteristics during storage. However, it has been found that ageing effects caused by reactions during storage can be minimized by keeping pyrolysis oil in cool places (Jahirul et al., 2014).

Although bio-oil from pyrolysis can be an effective alternate energy source, without upgradation direct applications of unprocessed pyrolysis oil is restricted due to its (Akhtar et al., 2012; Dickerson et al., 2013; Gollakota et al., 2016; Yildiz et al., 2016);

- High viscosity, water (18-25%, when feedstock moisture content is <10%) and oxygen contents (35-40%), HHV of about 17 Mj/kg and chemical instability
- Higher acidic nature (PH of 2-3) due to the organic acids, making it corrosive
- Solid (0.3-3%) and ash content including higher alkali metals whose depositions in combustion chambers or boilers decreases the efficiency of the equipment.

2.8 Bio-oil upgradation

The quality of oil can be steered with several mechanisms which involves the conversion of undesired chemical compounds or selective oxygen functionalities like carboxylic acid, ketones, PAH or aldehydes into more desirable compounds of alcohols, ethers and aromatics (Yildiz et al., 2016).

- a. **Hydro-treating**
- b. **Steam reforming**
- c. **Esterification**
- d. **Emulsification**
- e. **Supercritical extraction**
- f. **Co-pyrolysis**
- g. **Catalytic cracking**

2.8.1 Co-pyrolysis

Co-pyrolysis upgrades the quality of bio-oil besides its improved yield. This involves using a blend of two or more different substances as a feedstock (Abnisa et al., 2014).

A synergistic effect is the primary driving factor for all improvements in terms of oil quality and its yield. Not only is this, co-feeding biomass with higher H/Ceff feedstock such as plastics and WT found to promote aromatization with significant synergistic effect on HC production. Another benefit is that consumption of more waste as feedstock means that volume of waste into dumpsite can be reduced (Abnisa et al., 2014; Kim et al., 2017).

2.8.2 Catalytic Cracking

Catalyst addition in the pyrolysis process can improve bio-oil quality via off-line cracking or on-line catalytic cracking, using bio-oil or pyrolysis vapor as raw material (Abnisa et al., 2014). Catalyst mode of contact to its reactants can be applied at different positions in the process as (Jahirul et al., 2014; Yildiz et al., 2016);

- Its addition to the feedstock before putting in the reactor, to make it impregnated
- In-situ mode of operation where is added into the reactor already containing feedstock
- Ex-situ mode where catalyst is set in the secondary reactor to come in contact with primary pyrolysis vapors coming from upstream reactor

It is suggested that catalyst used should be stable, highly active, cheap, readily recyclable or regenerable, resistant to rapid deactivation by coke formation and with effective acidity and selectivity towards specific products (Dickerson et al., 2013; Yildiz et al., 2016). Applying in pyrolysis, catalyst decreases the optimal reaction temperature, lowers reaction time, enhances the diesel compounds production within 390-425°C boiling point range and increases selectivity towards gasoline products (Al-Salem et al., 2017). Usually it is observed in previous studies that catalyst addition lowers the oil production, which is explained by increase in gas vapor residence time in the reactor as they get the increased path to travel via catalyst particles (Liu et al., 2016). It is considered that an ideal catalyst not only gives optimum yield of bio-oil but upgrades its composition with enhanced H/C ratio, reduced oxygenated compounds, water and other undesirable products while maintaining its thermal strength and resisting deactivation (Lappas et al., 2012). Quality of bio-oil is enhanced through various catalytic reactions namely cracking, deoxygenation reactions which includes dehydration, decarboxylation, and decarbonylation, dehydration reactions like hydro-deoxygenation and hydrogenation, other reactions as aromatization, oligomerisation, polymerization, alkylation, isomerization and cyclization (Dickerson et al., 2013; Garba, 2017).

- **Types of Catalyst**

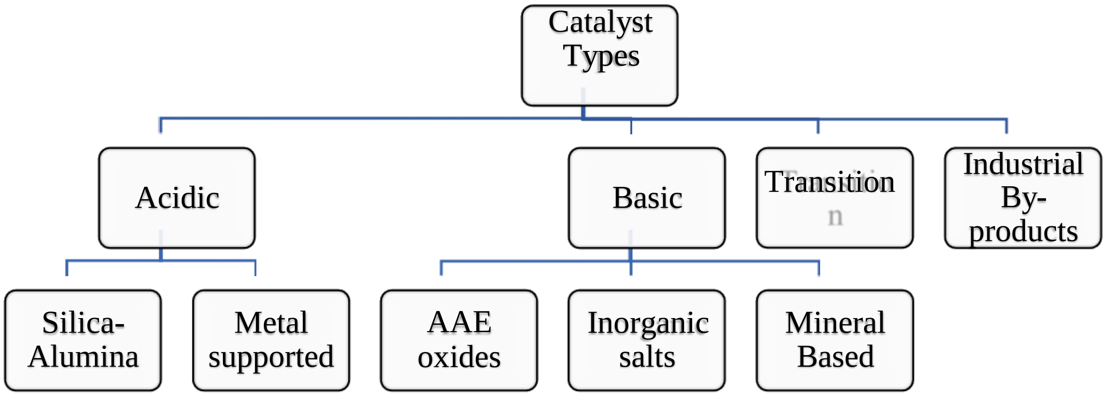

Figure 2.1 Catalyst types

a. **Acid catalyst**
b. **Base catalyst**
c. **Industrial byproducts**
d. **Transition metal oxide**

a. Acid catalyst

Acidic catalyst is synthesized from zeolite, noble metal oxides, metal oxides in sulphated form, and supported metals by doping or impregnation. Such catalyst increases the aromatic HC yield by cracking oxygenated compounds present in bio-oil.

i. Silica-Alumina catalyst

Various natural and synthetic zeolite catalyst such as HZSM-5, ferrierite, β-zeolite, HY, H-mordenite, ZSM-5 and other inexpensive materials like sepiolite, entonite have all shown to upgrade oil quality, however HZSM-5 has outperformed in various research studies yielding maximum amount of aromatics with least coke deposition. Among different silica-alumina catalyst, HZSM-5 is therefore widely used in pyrolysis of biomass as it has following properties

- 3D network of intra-pore structure with intermediate size of 0.5-0.5 nm that makes maximum surface area for catalytic activity
- Thermally and hydrothermally stable
- Shape selectivity and ion-exchange properties
- Hydrogen transfer ability that ultimately leads to higher HC production

b. Base catalyst

Strong basic catalyst such as amine substituted ZSM-5 have been known to be synthesized at high temperature, giving selectivity and reaction pathways as followed by base catalyst. It is to be noted that high temperature pre-treatment is necessary for generating active sites which removes absorbed CO_2, H_2O and sometimes O_2, enabling base catalyst to follow activity for organic reactions (Garba, 2017; Lappas et al., 2012).

i. Alkali metal and alkaline earth metal oxides

These metal oxides like CaO or MgO are definitive base catalyst comprising of oxide cations that makes up Bronsted base and metal anions functioning as Lewis acids. AAE oxides are known to upgrade bio-oil composition by reduced oxygenates, phenolic compounds, linear aldehydes, minimum acid production and increased formation of aromatics, lighter HC and cycloalkanes. Such improvement in oil quality is brought up by typical base catalytic reactions of ketonization, decarboxylation and deoxygenation. Out of other metal oxides, CaO use is appreciated much more due to its cost effective production from natural sources like limestone, slaked lime and its comparatively high basic strength (Garba, 2017; Liu et al., 2014; Zabeti et al., 2009). Catalytic Pyrolysis of sugarcane bagasse with different metal oxides observed that CaO catalyst loading of 5 and 10% decreased the reaction temperature to maximum content i.e. 496 °C from 532 °C. Moreover, it was inferred that CaO or MgO react with water to make basic solution, that influences hydrogen formation and therefore increases gas yield (Kuan et al., 2013).

2.8.3 Different catalyst combination

It has been investigated that pore size of the catalyst plays a crucial role in end-product composition and distribution. Most widely used zeolite catalyst with specific pore size distribution affects the aromatic yield. Generally, it is observed that zeolites with small size of pores mainly produce Carbon monoxide, Carbon dioxide and coke. In a study, medium pore size distribution 0.5-0.6nm of zeolite showed higher aromatic and oxygenate yield than other pore sized zeolite and on the other hand larger pores promoted the production of coke (Garba, 2017; Liu et al., 2014).

This has focused attention towards implying dual pore sized catalyst combination that makes the vapors to pass through larger pore range first, followed by smaller pores passage. As in a recent study, Al-SBA-15 catalytic ability was compared with MZSM-5, later one possessing both micro and mesopores along with its stronger acidity resulted into almost three times greater production of aromatic HC than Al-SBA-15 (Kim et al., 2017).

Furthermore, zeolite catalyst is used with AAE in recent studies that not only presents the advantage of wider pore size range but also acid and basic active sites give synergistic effect in upgrading the bio-oil to fuel grade. Most commonly used combination of catalyst mixture is HZSM-5 with alkaline earth metal oxides such as

MgO and CaO in dual catalytic stage bed. Some of the recent studies carried out are listed in the Table 2.2 verifying that such configuration has shown to increase aromatic yield, C-H bonds, decrease oxygen content and other undesirable products (Garba, 2017). One of the research results depicted synergistic effects in terms of minimum char production (by ~12%), henceforth favoring oil and gas formation, when HZSM-5 catalyst was applied in conjunction to MgO (Fan, Chen, et al., 2017). Generally, such bed makes the vapors to pass through basic catalyst first which converts initially decomposed biomass vapors into lighter HC fuel precursors which then undergoes acidic catalyst sites to be converted into desirable MAH (Zhang et al., 2013). It is discerned that dual catalyst bed not only elevates valuable aromatic HC formation but as well as influences the aromatic selectivity in the product oil (Wang, Zhang, et al., 2017). Inferred from the result of pyrolysis that was carried out using bi- functional HZSM-5/CaO catalyst, microporous HZSM-5 deactivation by coke deposition was minimized by CaO mesoporous structure that promoted the fragmentation of large heavy oxygenated compounds into lighter intermediate compounds, which otherwise gets deposit on surface of HZSM-5 (Liu et al., 2016).

Table 2.2 Acidic HZSM-5 and basic catalyst combined use in pyrolysis

Feedstock	**Catalyst**	**Mode of Operation**	**Temp °C**	**EHI**	**FBR**	**F:C**	**O:HZSM-5**	**Result**	**Ref**
Corn stover **&** **scum**	HZSM-5, CaO	In-situ	450, 500, 550, 600, 650	1	1:1	1:1	1:1	At 550°C max bo-oil yield of 29%, with max weight % of aromatics 83.7%	(Liu et al., 2016)
			550	1	1:1		1:0, 4:1, 2:1, 1:1, 1:2, 1:4, 0:1	At 1:4 max bio-oil yield of 38% with aromatics max wt% of 35.8	
			550	0.1, 0.5, 0.7, 1, 1.2, 1.4, 1.3	1:0, 4:1, 2:1, 1:1, 1:2, 1:4, 0:1		1:1	At 1:2 (1.2) max vio-oil 31.4% and aromatic yield of 29.3% wt	
Bamboo residue **&** **Waste lubricating oil**	HZSM-5, MgO	Ex-situ dual stage	500, 550, 600, 650, 700	-	-	1:2	-	600°C with max phenols & furans and peak area for aromatics	(Wang, Zhang, et al., 2017)

2.9 Analytical techniques

2.9.1 Gas Chromatography-Mass Spectrometry (GC-MS)

Gas Chromatography-Mass Spectrometry (GC-MS) can be used to study liquid, gaseous or solid samples. Analysis begins with the gas chromatograph, where the sample is effectively vaporized into the gas phase and separated into its various components using a capillary column coated with a stationary (liquid or solid) phase. The compounds are propelled by an inert carrier gas such as helium, hydrogen or nitrogen. As components of the mixture are separated, each compound elutes from the column at a different time based on its boiling point and polarity. The time of elution is referred to as a compound's retention time. GC has the capacity to resolve complex mixtures or sample extracts containing hundreds of compounds.

Once the components leave the GC column, they are ionized and fragmented by the MS using electron or chemical ionization sources. Ionized molecules and fragments are then accelerated through the instrument’s mass analyzer, which quite often is a quadrupole or ion trap. It is here that ions are separated based on their different mass-to-charge (*m/z*) ratios. GC-MS data acquisition can be performed in either full scan mode, to cover either a wide range of *m/z* ratios, or selected ion monitoring (SIM) mode, to gather data for specific masses of interest.

The final steps of the process involve ion detection and analysis, with fragmented ions appearing as a function of their m/z ratios. Peak areas, meanwhile, are proportional to the quantity of the corresponding compound. When a complex sample is separated by GC-MS, it will produce many different peaks in the gas chromatogram and each peak generates a unique mass spectrum used for compound identification. Using extensive commercially available libraries of mass spectra, unknown compounds and target analytes can be identified and quantified (Chuahan et al. 2014; Shin et al. 2011).

2.9.2 X-ray Fluorescence (XRF)

XRF (X-ray fluorescence) is a non-destructive analytical technique used to determine the elemental composition of materials. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays (a fingerprint) that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition (F. L'Annunziata et al., 2016).

A solid or a liquid sample is irradiated with high energy X-rays from a controlled X-ray tube. When an atom in the sample is struck with an X-ray of sufficient energy (greater than the atom's K or L shell binding energy), an electron from one of the atom's inner orbital shells is dislodged. The atom regains stability, filling the vacancy left in the inner orbital shell with an electron from one of the atom's higher energy orbital shells. The electron drops to the lower energy state by releasing a fluorescent X-ray. The energy of this X-ray is equal to the specific difference in energy between two quantum states of the electron. The measurement of this energy is the basis of XRF analysis (JA. Plant et al., 2014).

2.9.3 Brunauer-Emmett-Teller (BET)

Brunauer-Emmett-Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of materials. BET theory applies to systems of multilayer adsorption, and usually utilizes probing gases that do not chemically react with material surfaces as adsorbates to quantify specific surface area. Nitrogen is the most commonly employed gaseous adsorbate used for surface probing by BET methods. For this reason, standard BET analysis is most often conducted at the boiling temperature of N_2 (Nasrollahzadeh et al. 2019).

Before measurements, the samples were degassed in vacuum at 200 ^oC for at least 6 h. BET equation uses adsorption data in a relative pressure range from 0.04 to 0.2 to determine the specific surface area. By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions can be derived from the adsorption branches of isotherms, and the total pore volumes (V_t) will be estimated from the adsorbed amount at a relative pressure P/P_0 of 0.992 (Liu et al. 2007).

Materials and methods

3.1 Feedstock

3.1.1 Preparation

RS was collected from Faisalabad division, Punjab, Pakistan. Biomass was first sun dried for 24 hrs to remove the moisture and grinded in a milling machine followed by sieving to attain a size of 0.4-1.8 mm. Reinforced fabric and steel cord free heavy vehicle WT was obtained from a local vendor in Rawalpindi, Pakistan and was shredded to obtain particle size as that of biomass. WT was oven dried at temperature 105 ℃ for 24 hrs to remove the moisture.

Figure 3.1 RS and WT used in the reaction

3.1.2 Characterization

Ultimate and proximate analysis of samples were performed according to standard procedure described by the ASTM D5291-96 and ASTM D3172-07 respectively. Carbon, Hydrogen and Nitrogen percentage were determined using 5E-CHN2200 CHN analyzer while 5E-IRS 11 analyzer was used for Sulphur content determination. Meanwhile, oxygen content was quantified by difference (Razzaq et al. 2019). The percentage of hemicellulose, cellulose and lignin of biomass was determined following the procedure published in previous literature (Qu et al. 2011). Calorific values of WT and biomass were obtained using 6200 Isoperibol Oxygen Bomb

Calorimeter following standard procedure (ASTM D5865-13). Moreover, to study the thermal stability of feedstock, thermogravimetric analysis (TGA) of WT and RS was performed using TGA 5500 at heating rate of 20 °C/min. in an inert atmosphere.

3.2 Catalyst

3.2.1 Preparation

Both basic oxide catalysts, CaO and MgO, were purchased in granular shape with average particle size 2 mm. Ammonium ZSM-5 having Silica to Alumina ratio (SiO_2/Al_2O_3) of 38 were bought in pallets form, which was subjected to calcination at 500 °C for 5 hrs in order to convert it into HZSM-5 (Zambare et al. 2019). HZSM-5 pallets have cylindrical shape with 1 mm width and 5 mm depth

Figure 3.2 CaO, MgO and HZSM-5 catalyst

3.2.2 Characterization

The pore characteristics and surface features of the catalysts were analyzed by a Micromeritics Gemini VII adsorption instrument with N_2 at 77 K (J. Wang et al. 2017). BET method was used to determine the specific surface area. T-plot method was utilized to find the microporous volume (V_{micro}), total pore volume (V_t) was obtained by measuring the gas adsorbed at relative pressure (P/P_o) 0.99, and mesoporous volume was found by subtracting micro pore volume from total pore volume. Composition of catalysts were identified using XRF spectrometer (JSM-3202M of Jeol), fitted with X-ray tube of Rhodium anode and Silicone Lithium (Si-Li) detector.

3.3 Experimental Set-up

3.3.1 Reactor and other accessories

Overall schematic diagram of the process is shown as Figure 3.3. A cylindrical (length of 50.4 cm and internal diameter of 10.8 cm) fixed bed pyrolizer (R1), fabricated with stainless steel (SS), was used as main reactor to perform pyrolysis experiments. A secondary stainless steel cylindrical catalytic reactor (R2) (length of 36 cm and internal diameter of 4.2 cm) was installed right above the R1. An electric ceramic band heater was used to heat up the core of reactors. Considering high temperature of process, ceramic wool was wrapped around the reactors as insulating material (Gellert 2010). The wool layer was kept intact with thermal bandage. K-type thermocouple was fixed in reactors' top flange reaching to center of feedstock and catalyst bed to monitor the actual reaction temperature. A proportional integrated derivative (PID) controller was used to control and maintain the heating rate (20°C/min) until final pyrolysis temperature of 500 °C was achieved. R2 was followed by condenser in which ice-water mixture added with common salt (NaCl) was used as cooling medium. Addition of common salt lowers the ice the temperature and enhances cooling.

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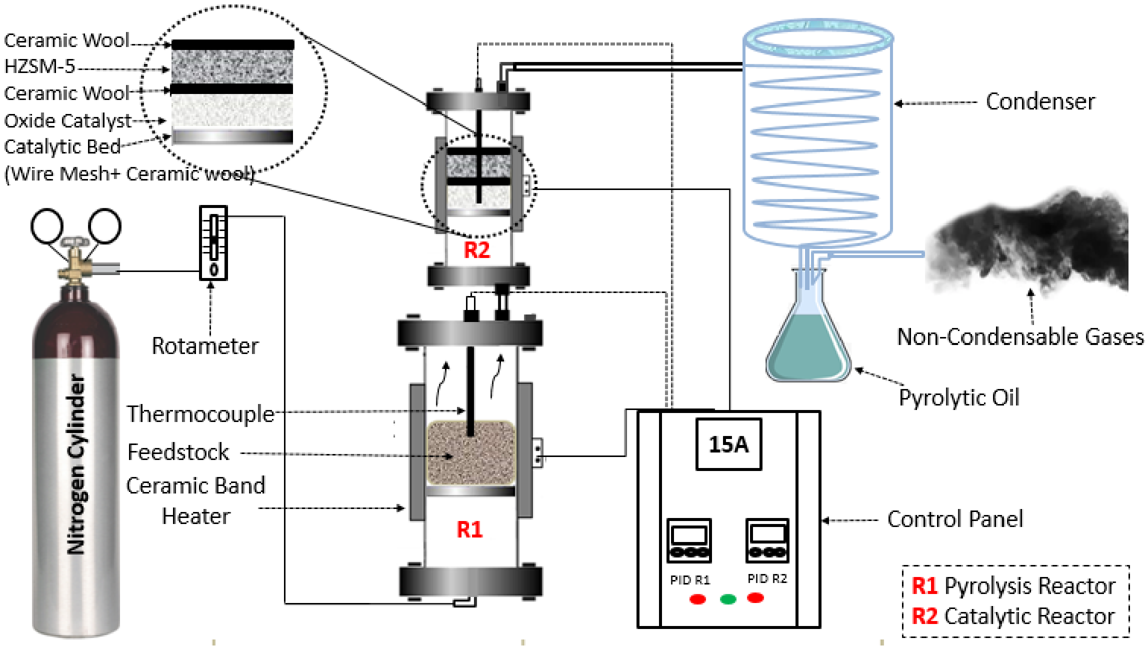

Figure 3.3 Schematic diagram of Pyrolysis Setup

3.3.2 Experimental test Procedure

A 100 g sample was loaded into R1 for each batch run. Blend ratio adopted for co pyrolysis of RS and WT (RS/WT) was 1:1. Feedstock to catalyst ratio was also adopted as 1:1 for the whole study, therefore a total of 100 g of catalyst was fed in R2 for every run. For experimental runs exploring dual catalytic bed, the catalytic bed was made by placing the metal oxide CaO/MgO (macro/mesoporous) catalyst granules before (microporous) HZSM-5. The two layers were isolated by a layer of ceramic wool. To ensure the stability of catalyst bed ceramic wool was also placed at its top and bottom. Prior to the heating of reactors, N_2 gas with constant flow rate of 500 cm^3/min. was passed through the system for 30 minutes to purge inside trapped air to avoid combustion of feedstock. Initially the R2 temperature was raised to 550 °C, then the heater of reactor R1 was turned on to achieve the final pyrolysis temperature of

500 °C. Two series of experiments were performed, keeping CaO/HZSM-5 and MgO/HZSM-5 at 1:0, 3:1, 1:1, 1:3 and 0:1. Condensate was collected in conical flask fitted downstream of condenser. After each batch run completion, char was removed once reactor was cooled down to room temperature and weighed. The mass of oil was quantified from difference of mass of conical flasks before and after pyrolysis. In addition, yield of non-condensable gases was calculated by subtracting mass of oil and char from the initial mass of feedstock. Pyrolytic oil produced consisted of AP and OP which were then separated using separating funnel. However, oil produced from WT contained only OP and didn't need any further processing for phase separation. Each experimental run was performed at least 3 times to ensure reproducibility.

Table 3.1 Experimental series

		Metal oxide to HZSM-5 ratio				
Series 1	HZSM-5:CaO					
Series 2	HZSM-5:MgO	1:0	3:1	1:1	1:3	0:1

3.4 Liquid product analysis

3.4.1 Chemical analysis

Chemical composition of oil was determined by using Shimadzu QP2020 gas chromatography/mass spectrometer (GC/MS), equipped with the column (DB-5 MS at 30 m × 0.32 mm and 0.25 µm). The initial column temperature was kept at 30 °C for 2 min and then increased to 290 °C at a rate of 10 °C/min, then held constant at 290 °C for 20 min. The vaporizer temperature was 290 °C and the sample volume was 1 µL with a split ratio of 1:80. Helium was introduced as a carrier gas at a flow rate of 1.47 mL/ min. Obtained chromatograms identified the organic compounds by comparing them with those from the National Institute of Standards and Technology (NIST) mass spectral data library. A semi-quantitative technique was used to analyze the relative proportion of each compound in liquid oil.

3.4.2 Physical analysis

Physicochemical characteristics of oil product including density, pour point, flashpoint, kinematic viscosity, specific gravity and HHV were obtained following the respective standard procedures of ASTM and IP. Flash point was measured by ASTM D7236 standards using Pensky-Martens closed-cup flash tester K16000. Pour point was determined following ASTM D97 standards by using Koehler instrument company equipment. Density and specific gravity were analyzed by ASTM D4052 and ASTM D4052-96 respectively. Whereas, kinematic viscosity and HHV were determined following ASTM D244 and ASTM D240 standards by using redwood viscosity meter and 6200 PARR isoperibol bomb calorimeter respectively (Muneer et al. 2019).

Result and discussion

4.1 Feedstock analysis

Proximate analysis of RS and WT exhibit high volatile content i.e. 70.8 wt% and 65.7 wt% respectively. Greater the volatile matter in feedstock is indication of higher potential for harnessing energy in the form of bio oil. RS has comparatively higher ash and moisture content whereas, WT possesses higher fixed carbon content. Among these parameters, volatile solids and ash content are crucial factors in determining quality and quantity of pyrolysis oil yield. High ash content diminishes yield of bio-oil, increasing char yield and non-condensable gases. In addition, moisture in substrate decreases the efficiency of process and calorific value of products (Jin et al. 2019). As shown by ultimate analysis results, Carbon content in RS and WT is 41.4 wt% and 85.3 wt% respectively. Higher Carbon and hydrogen content in WT is likely to increase the HC content of oil which will consequently enhance the calorific value of liquid oil (Shah et al. 2019). The pyrolysis final products also depend on the composition of biomass. RS is rich of cellulose component. Cellulose plays an important role for better quality oil production (Kim et al. 2017). Lignin (14.4 wt%) is also present in RS which usually produce phenols and aromatics in oil in the presence of zeolitic catalyst (Qu et al. 2011). However, polyphenols are considered carcinogens in bio oil.

Table 4.1 Feedstock analysis

Proximate Analysis	**WT**	**RS**
Moisture	1.5	5.1
Volatile Matter	65.7	70.9
Fixed Carbon	28.4	13.6
Ash	4.5	10.5
Ultimate Analysis (.wt%)		
C	85.3	41.4
H	7.7	5.1
N	0.6	0.9
S	1.1	-
O[a] (by difference)	0.8	42.4
Component Analysis (.wt%)		
Hemicellulose	-	25.2
Cellulose	-	40.3
Lignin	-	14.4
Calorific Value (MJ/kg)		
	38.1	17.9

[a] Calculated by difference (ash mass is included)

TGA and DTG analysis of WT and RS are shown in Figure 4.2. In case of RS, the first degradation phase started at room temperature and continued up to 130 °C due to removal of moisture content, followed by hemicellulose degradation at around 230 °C and cellulose degradation 310 °C (Williams and Besler 1993). Lignin ,due to its complex structural matrix, was degraded beyond temperature of 400 °C (Jin et al. 2019). DTG (Figure 4.2b) curve shows that highest mass loss rate for RS occurred around 330 °C (Jin et al. 2019). Degradation of WT started around temperature of 270 °C at which natural rubber (NR) decomposed which was followed by degradation of styrene butadiene (SBR) and butadiene rubber (BR) in later step. Maximum degradation leading to significant weight loss of 47.5 wt% was between 270 and 450 °C which is in line with previous reports (Azizi et al. 2019). DTG curve shows two peaks for WT mass loss first at 380 °C for the decomposition of NR and second peak at 445 °C for the thermal decomposition of SBR and BR (Elbaba et al. 2010). Hence final temperature of pyrolysis was set around 500 °C.

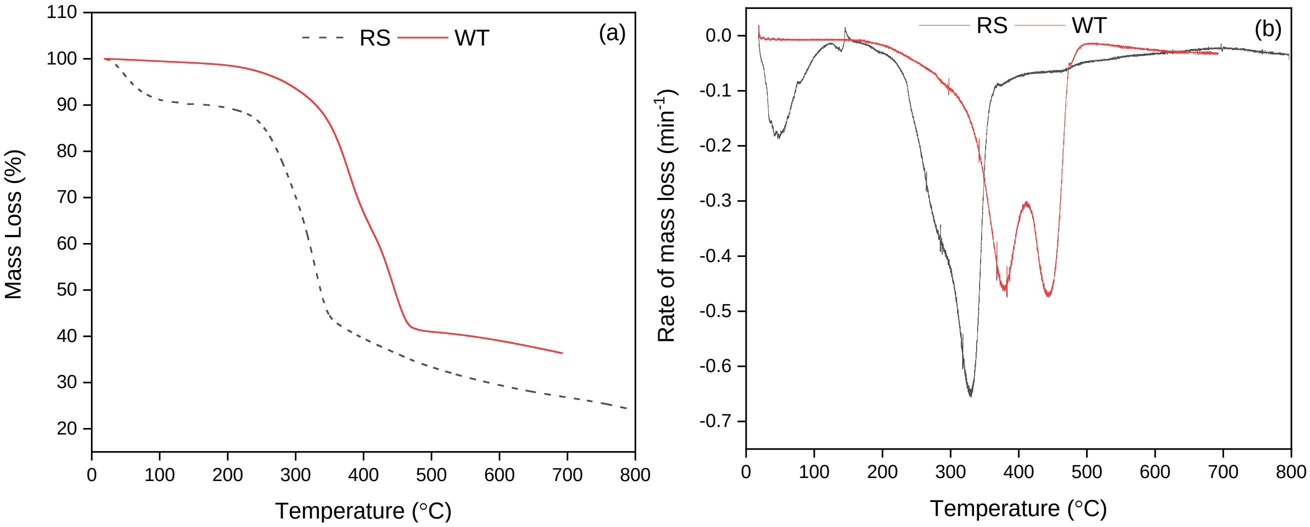

Figure 4.1 TGA (a) and DTG (b) profile of WT and RS

4.2 Catalyst analysis

XRF results for the catalysts are given in the Table 4.2, showing compounds present in substantial quantities. The Si and Al content were present in major quantities in HZSM-5. These compounds affect the cracking efficiency of catalyst (Kyaw, Su, and Hmwe 2015). While the oxide catalysts have minute quantity of Si. Table 4.3 presents the BET parameters of Catalysts. BET surface area was highest for HZSM-5 and possessed higher micro-pore volume whereas micro-pores were absent in CaO and MgO catalysts rendering their structure mesoporous.

Table 4.2 XRF analysis of the catalysts

Catalysts	Chemical Contentwt%				
	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3
HZSM-5	96.1	3.0			
MgO	1.0	–	0.2	98.3	0.5
CaO	2.7	–	96.3	–	0.6

Table 4.3 Surface and textural properties of catalyst

Catalyst	**BJH**	**Surface Area m^2/g**	**Porosity cm^3/g**

	Average Pore size nm	BET	V_{Total}	V_{meso}	V_{micro}
HZSM-5	1.4	282.9	0.105	0.044	0.06
MgO	27.9	33.1	0.234	0.232	UD
CaO	45.1	10.9	0.123	0.121	UD

[a]UD undetectable

4.3 Effect of Catalysts on end product yield

Catalyst influenced the variations in product yield distribution as shown in Figure 4.2. Incorporation of individual and combination catalyst proved neutral for char production and yield of pyrolysis oil, but negative for gas yield. Maximum liquid yield for catalytic pyrolysis was observed for MgO i.e. 43 wt% while lowest yield was observed for HZSM-5:CaO ratio of 3:1. Low yield might be due to reaction of volatiles generated from preliminary pyrolysis with active sites on catalyst causing more degradation of oxygenous compounds to H_2O, CO_2 or light HCs (Zhang et al. 2018). Reaction of volatiles with acidic sites in catalyst promote decarboxylation, decarbonylation and dehydration leading to lower pyrolysis oil yield (Muneer et al. 2019).

OP production decreased in presence of catalyst while AP increased. This trend was also observed in previous studies (Iftikhar et al. 2019; Stefanidis et al. 2011). Iftikhar et al. (2019) reported similar changes in product distribution while studying the influence of HZSM-5, MgO and CaO catalyst on co-pyrolysis of sugarcane bagasse with polystyrene. Gaseous yield decreased slightly in case of catalytic pyrolysis, which can be attributed to the presence of catalytic bed subjected to thermal cracking resulting in the coke formation. Oil yield in case of individual HZSM-5 was 40 wt% which decreased when set in combination with CaO, this is due to the increase in the residence time of gases in the presence of CaO while the vapors pass through HZSM-5 easily due to its three dimensional porous structure (Dickerson and Soria 2013). Maximum oil yield for dual catalyst experiment runs was 39.5 wt% for HZSM-5:CaO of 1:3 which gradually decreased with decreasing quantity of CaO to 36.7 wt% for HZSM-5:CaO at 3:1. This finding was in contrast with Liu et al. (2016), who studied the influence of CaO and HZSM-5 as catalyst on the co-pyrolysis of corn stover and scum for bio-oil production and observed the decreased bio-oil yield with the addition of CaO catalyst. However, the finding was in accordance with Iftikhar et al. (2019) and Lin et al. (2010) who reported an increase in oil yield with increase in CaO:HZSM-5 in their respective studies.

By Adding HZSM-5 to MgO, bio oil yield decreased from 43 wt% (for MgO only) to 39 wt% for HZSM-5:MgO at 3:1. Iftikhar et al. (2019) also reported decrease in bio oil yield from 45 wt% (MgO only) to 35 wt% at HZSM-5:MgO ratio of 3:1. A similar study investigating catalytic co-pyrolysis of lignin and LDPE, reported higher oil yield with increased MgO content when used in combination with HZSM-5 (Fan et al. 2016). Potential reason for this trend was enhanced alkylation (due to MgO) leading to phenol formation thus increasing bio oil yield.

For dual catalyst, increasing the loading of HZSM-5 catalyst, decreases the oil yield. The liquid yield was higher in case of HZSM-5/MgO in comparison with HZSM-5/CaO. The maximum oil yield in case of HZSM-5/MgO was 40 wt% at 1:3. One possible explanation for decrease in oil yield for dual catalyst is that the vapors have to pass through the catalysts which increases the residence time, favoring secondary thermal cracking (Iftikhar et al. 2019; Liu et al. 2016).

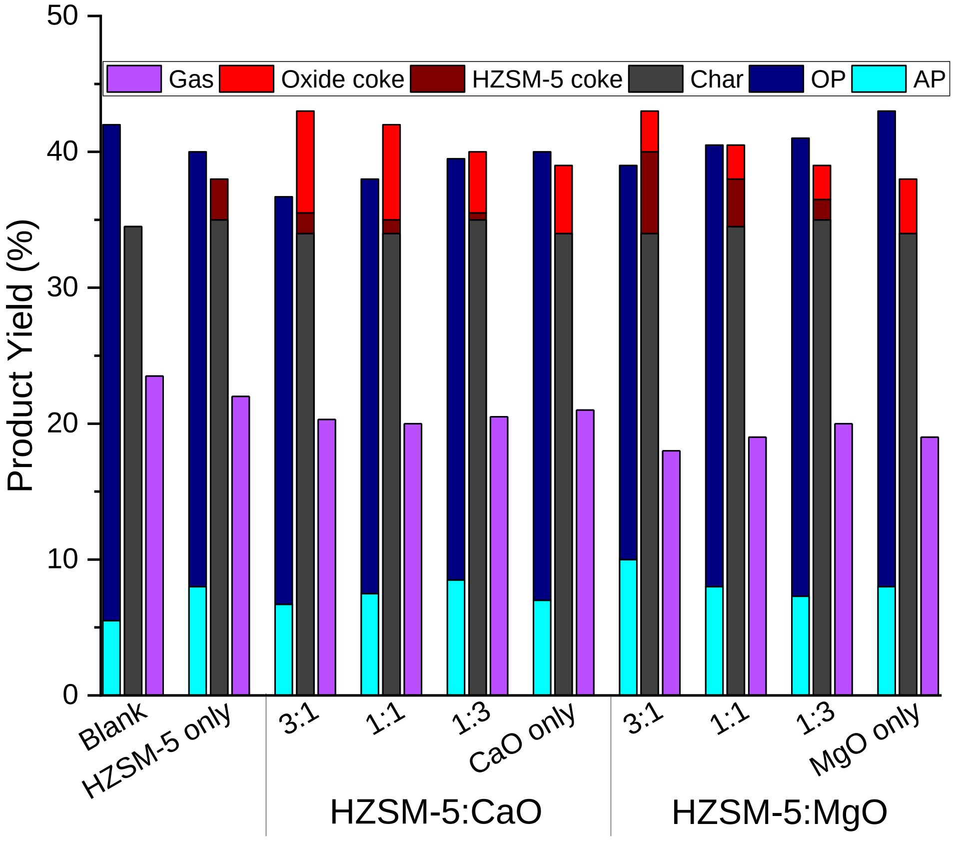

Figure 4.2 Product yield distribution for non-catalytic and catalytic co-pyrolysis

4.4 Effect of Catalyst on oil quality

4.4.1 GC-MS analysis of oil

Figure 4.3 shows the catalyst induced variation in composition of oil yield as observed in GC-MS analysis. Oil samples obtained in the experimental runs without involving catalyst as well as those involving HZSM-5, MgO and CaO alone and their combinations, were also analyzed for comparison. Bio-oils generally contain hundreds of organic compounds due to their complex nature. Therefore, they were divided in four main classes namely MAHs, PAHs, aliphatic HCs and oxygenates. OP obtained in non-catalytic co-pyrolysis contained low aromatic HCs and high (RS originated) oxygenates. However, the oil produced by different catalyst combinations mainly consisted of aromatic and aliphatic HCs along with reduced quantities of oxygenates. The reduced oxygenates indicate lower amounts of unwanted phenols, ketones, ester, aldehydes and ethers which lead to instability of bio oil and reduce the heating value. In case of single catalytic pyrolysis, minimum oxygenates were produced by MgO while the maximum, for CaO. The aliphatic HCs mainly consisted of cycloalkanes, alkanes and alkenes which are considered good for transportation fuel (Hellier et al. 2018). Aromatics on the other hand improve octane number of fuel, improving its combustion characteristics(Seames et al. 2017). The PAHs mainly comprised of naphthalene and anthracene whereas, MAHs included benzene, toluene, styrene and other derivatives. PAHs are carcinogenic that can sustain for longer periods of time in environment, are formed by secondary reactions of benzene derivatives at high temperature (~550°C to 650°C) so it is recommended to carefully regulate temperature during pyrolysis (Liu et al. 2016).

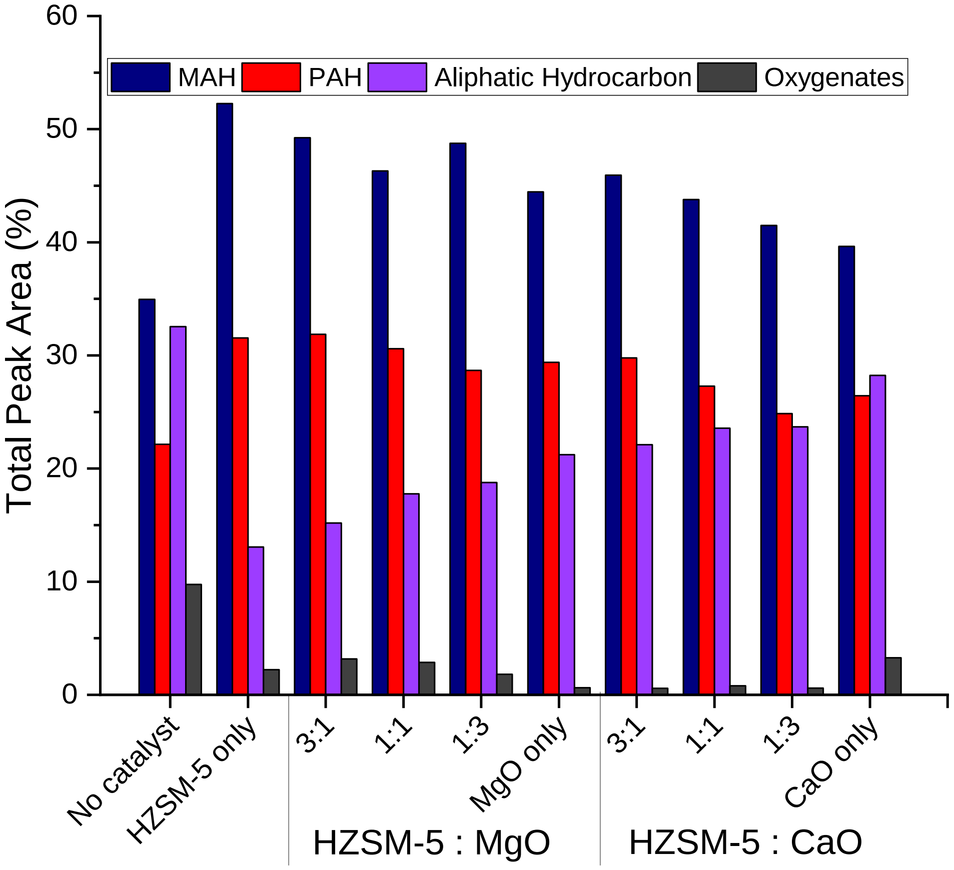

Figure 4.3 GC-MS results of oil samples obtained
in non-catalytic and catalytic co-pyrolysis

The aromatic HC content was maximum for HZSM-5 catalyst compared to MgO and CaO, corroborating the previously reported findings.Presence of acid sites are favorable to the aromatization reaction ,and pore size of HZSM-5 resembles to the kinetic diameters of aromatics which benefits the production of HC pool species (Jae et al. 2011).Similarly, the highest aliphatic HC content was observed for CaO as a catalyst.

Furans and phenolic compounds preferably decreased through the incorporation of single and combination catalyst. Minimum oxygenates were observed for HZSM-5:CaO ratio of 3:1, giving off 94.2 wt% less oxygenates compared to non-catalytic pyrolysis. In case of single catalysts, MgO aided catalytic pyrolysis gave 91.3 wt% less phenols and 96.5 wt% less furans. However, in case of combination catalysts, maximum decrease in phenols were observed for HZSM-5: CaO ratio of 1:1.

Variations in MAHs and PAHs content caused by various combinations of catalysts is presented in Figure 4.3. Optimum yield of MAH (45.9 wt%) for combination of HZSM-5 and CaO was achieved at ratio of 3:1 however, increase of CaO in combination catalysts resulted in gradual reduction of MAH and lowest content was observed for ratio of 1:3 (41.5 wt%). PAH followed the similar trend and their content reduced from 29.8 wt% (3:1) to 24.8 wt% (1:3). It is to be worth mentioning that HZSM-5 produces more MAH alone compared to its any combination with CaO nevertheless this was accompanied by the highest malign PAH content. Besides, combinations with CaO found to more efficient in deoxygenation of oil compared to HZSM-5 alone. This could be elucidated on the following grounds; pyrolytic vapors initially pass through mesoporous CaO where heavier oxygenated compounds are transformed into lighter compounds; facilitating their influx into cavities of microporous HZSM-5 and consequent conversion into aromatic compounds through various reactions (Liu et al. 2016). In case of combination of HZSM-5 with MgO, indefinite trend was observed. At HZSM-5:MgO of 3:1 and 1:3, aromatic yield was nearly identical and relatively higher compared to (1:1). In addition, increasing MgO content in combination also increased aliphatic content possibly due to effect of pore size of MgO advocating olefins production while HZSM-5 effectively transformed long chain HCs to aromatics via cracking and other reactions (Fan et al. 2017). MgO addition also reduced oxygenates due to enhanced deoxygenation, de-acidification and aldol condensation, converting acids and carbonyl compounds into ketones. The active sites of HZSM-5 convert these HCs into gasoline like compounds through ketonization and aromatization (J. Wang et al. 2017). These results indicate that dual catalyst bed having acid and basic reaction sites improved the performance and led to generation of oil of high quality and yield compared to HZSM-5 or oxides (MgO and CaO) alone. Among all combination of HZSM-5 with either of oxides, HZSM-5:MgO ratio of 1:3 produced highest amount of MAHs (48.7 wt%) and lowest unwanted PAHs (28.7 wt%). Moreover, MAH and PAH yield for any combination of MgO remained higher compared to respective combination of CaO with HZSM-5. This attributes that, MgO improved the oil quality considerably as compared to CaO when used in dual catalyst bed with HZSM-5.

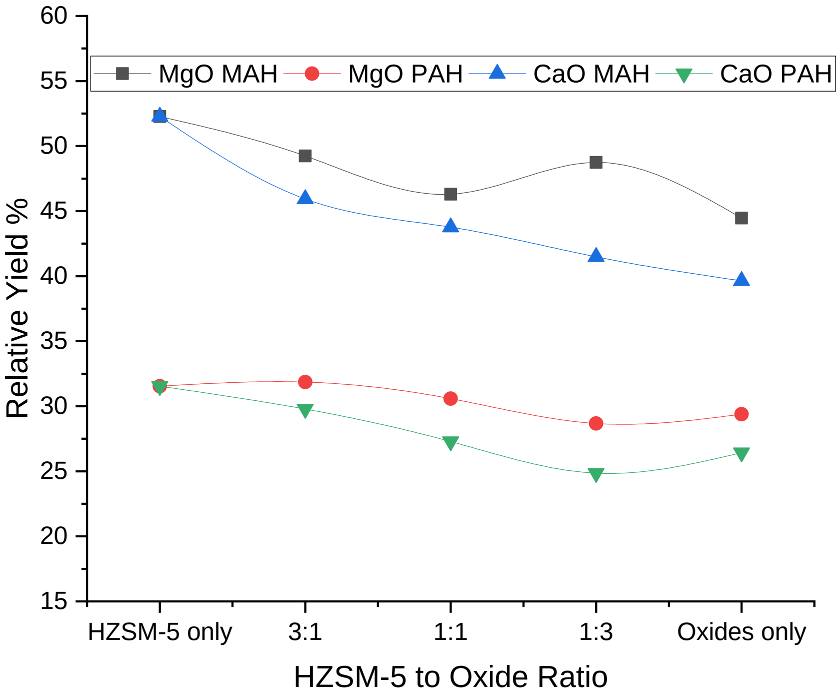

Figure 4.3 Aromatic HCs selectivity in various combinations of catalysts

4.4.2 Physical properties of oil

Physical characteristics of pyrolysis oil are shown in Table 4.4. For comparison purposes, characteristics of conventional (diesel) fuel are also listed in the table. Pour point of all oil samples was found to be less than −40°C indicating its potential use on colder regions as fuels having higher pour point tend to form wax leading to longer engine start up time and causing blockage of filter and fuel system. Flash point of the oil samples was found to be very low which is attributed to high amounts of volatiles and aromatic compounds. Low flash point of fuels necessitates extra safety precautions in handling and storage (Muneer et al. 2019). The flash point of oil can be increased by using additive Alpha Terpineol through blending. By addition of 12-14 % terpineol increases the flash point by 50 °C to 60 °C (Talbott, Falls, and Us 2002).

Calorific value (HHV) is the most important parameter of fuel influenced by the hydrogen and moisture content. Calorific value of bio-oil was increased from 15.6 MJ/Kg for RS to 36.1 MJ/Kg for WT-RS. HHV of WT obtained pyrolytic oil was 41.5 MJ/Kg, due to higher H/C_{eff} ratio. Catalyst application in co-pyrolysis improved HHV value of product oil which were comparable to values of diesel. Catalytic co-pyrolysis significantly improved the density of bio-oil, however it is slightly higher than the conventional diesel. Kinematic viscosity of product oil from pyrolysis of RS decreased by WT addition and in presence of dual catalyst bed. Low kinematic viscosity is favored as they cause easy atomization of fuel when diffused in combustion chamber causing improved engine performance (Kim, Agblevor, and Lim 2009). When dual bed catalyst was employed, kinematic viscosity was decreased by 14.6 %, bringing the fuel quality relatively closer to diesel. Moreover, HHV value was also close to diesel indicating its potential use as transportation fuel.

Table 4.4 Physical characteristics of pyrolytic oil

Pyrolytic Oil	HHV (Mj/kg)	Density at 20^{o}C (g/cm^3)	Kinematic Viscosity at 40^{o}C (cSt)	Flash Point (^{o}C)	Pour Point (^{o}C)
Diesel	43.1	0.81-0.87	2-5	55-60	Max 18
RS	15.6	1.07	10.2	< -30	< -40
WT	41.5	0.93	3.1	< -30	< -40
Co-pyrolysis (without Catalyst)	36.1	0.94	5.3	< -30	< -40
HZSM-5:CaO 3:1	40.6	0.92	4.6	< -30	< -40
HZSM-5:MgO 1:3	40.7	0.91	4.6	< -30	< -40

Conclusions and Recommendations

5.1 Conclusions

Catalytic co-pyrolysis of RS and WT was conducted to analyze the dual catalytic performance of HZSM-5 with metal oxides (CaO/MgO) on pyrolytic oil quality. Dual catalytic bed significantly promoted the production of MAHs, while subsiding the unwanted products like PAHs and oxygenates. This is because of the fact that the pyrolytic vapors are first subjected to form Ketones and Furans by ketonization and deoxygenation reactions by passing through basic catalyst (CaO/MgO), ultimately converting them to aromatics by HZSM-5. Furthermore, HZSM-5: MgO optimal ratio of 1:3 yielded higher selectivity of MAH (48.7 wt%) and lesser undesirable PAH (28.7 wt%) in comparison to (45.9 wt% MAH and 29.8 wt% PAH) selectivity obtained by optimal 1:3 CaO:HZSM-5. This implies that, MgO enhanced the liquid oil quality to greater extent as compared to CaO, combined with HZSM-5. Moreover, the oil produced by dual catalytic bed has the quality closer to the conventional fuels.

5.2 Recommendations

- Natural Zeolite is recommended for future use as catalyst because of its availability and cheap cost
- Gas yield analysis should be carried out as it is a vital product
- Cost-benefit analysis for its practical application in field

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