Co-pyrolysis of Sugarcane Bagasse and Polystyrene with ex-situ catalytic bed of Metal Oxides / HZSM-5 with focus on liquid yield

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Certificate

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

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Abstract

Catalytic co-pyrolysis of sugarcane bagasse (SCB) and polystyrene (PS) was conducted in a fixed bed reactor over HZSM-5, metal oxide (MgO, CaO) and dual catalyst HZSM-5:CaO, HZSM-5:MgO combinations. Effect of microporous HZSM-5, mesoporous MgO and CaO and dual catalyst mass ratio on pyrolytic liquid yields and chemical composition of liquid organic phase (OP) was examined. Though the catalyst addition decreased the yield of liquid OP, general improvement in mono-aromatic hydrocarbon yield with least content of oxygenates was achieved in the catalytic trials compared to non-catalytic experimental runs. Results revealed that in comparison to metal oxides, acidic HZSM-5 showed maximum conversion efficiency of acids, furans and phenols presenting them as hydrocarbon source for aromatic production. Basic MgO when combined with acidic HZSM-5, was found to conduce better catalytic performance yielding improved oil quality compared to HZSM-5:CaO catalyst. Mass ratio of 1:3 HZSM-5:MgO exhibited most eminent synergistic effect with maximum (56.8wt.%) mono-aromatic hydrocarbon (MAH) yield and lowest (20.8wt.%) poly-aromatic hydrocarbon (PAH) content of. Additionally, increased calorific value and density upgradation comparable to standard diesel fuel quality was observed in the presence of dual catalyst layout.

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List of Abbreviation

HTC	Hydrothermal carbonization
HC	Hydrocarbons
HHV	High Heating Value
LHV	Low heating value
HDO	hydro-deoxygenation
PAH	Polycyclic Aromatic Hydrocarbon
MAH	Monocyclic Aromatic Hydrocarbon
AAE	Alkali and Alkaline earth metals
HDT	Hydrotreating
HDO	Hydrodeoxygenation
SCF	Supercritical fluids
FC	Fixed carbon
VM	Volatile matter
EHI	Effective hydrogen index
AC	Activated carbon
SCB	Sugarcane bagasse
PS	Polystyrene
SS	Stainless Steel
AP	Aqueous phase
OP	Organic phase
TGA	Thermogravimetric analysis
BET	Brunauer–Emmett–Teller

BJH	Barrett–Joyner–Halenda
DFT	Density functional theory
XRF	X-ray Fluorescence
F:C	feedstock to catalyst ratio
FBR	feedstock blend ratio
O:HZSM-5	Metal oxide to HZSM-5 catalyst ratio

Chapter 1

Introduction

1.1 Background

In the developing countries like Pakistan 12% of solid waste is composed of plastics (Hoornweg et al., 2012) out of which only 40% of waste plastic undergo secondary or mechanical recycling. Polystyrene in the plastic waste stream is found with minimum percentage of recycling due to collection constraints, its complicated processing and high recycling cost. Moreover, PS possess energy content as high as 37.2MJ/kg which is two times greater than that of coal (Kositkanawuth et al., 2014). This has facilitated tertiary recycling, making its use as a higher value hydrocarbon feedstock for plastic-to-fuel technologies A recent study conducted the pyrolysis of different plastic types and found PS showed maximum liquid oil production (80.8wt.%) with highest stability and aromatic hydrocarbon yield in comparison to other types of plastics (Miandad et al., 2017).

Along with hydrocarbon waste, agricultural residue including bagasse with high ligno-cellulosic content has been an attractive feedstock for second-generation fuel production. Being 5th largest producer in the world, Pakistan grow 50 million tons of sugarcane at a growth rate of 2.5% annually. It has been generalized that 27% of the crop's portion is recovered as bagasse, this makes the residue generation of about 14 million tons per annum in the country (Badshah et al., 2012; Valasai et al., 2017). As well as, bagasse production in Pakistan is higher compared to other countries owing to the increased fiber content in sugarcane i.e. 15-18% while the crop produced in other countries constitute 12-14% fiber only (Butt et al., 2013).

Catalytic co-pyrolysis of hydrogen deficient biomass as SCB with a high H/C_{eff} ratio waste, such as plastics, has shown to increase pyrolytic oil yield with enhanced production of aromatic hydrocarbon and value added chemicals. Feedstock of high Effective hydrogen index acts as a good hydrogen supplier, improving overall H/C_{eff} of total feedstock that promotes fine-tune performance of catalyst by suppressing coke formation. Various acidic, basic, industrial by-products and transition metals have been employed as catalyst in pyrolysis. However, in recent years' due attention has been given to investigate the effect of combined acid HZSM-5(microporous) and basic metal oxide (mesoporous) dual stage catalytic bed, on pyrolysis liquid oil production and its upgradation. Dual catalytic stage bed allows bio-oil vapors to pass through the bed of basic metal oxide catalyst first and then through HZSM-5 bed before leaving the reactor for condensation. Studies have found that application of HZSM-5 with AAE particularly MgO, CaO 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. Research carried out on fast microwave-assisted co-pyrolysis in the presence of HZSM-5 and MgO catalyst, depicted that LDPE with high H/C_{eff} ratio removed the side functional groups and decreased char formation during lignin pyrolysis process. Optimized ratio combination of the bi-functional catalyst showed the improved production of aromatics by zeolite and alkylation of phenols by magnesium oxide (Fan, Chen, et al., 2017). The results of the investigation on pine sawdust catalytic pyrolysis demonstrated that increased cracking catalyst addition (MgO, CaO or FCC) in acid catalyst(HZSM-5) exhibited an increasing trend of aromatic formation. It has been explained by enhanced production of light oxygenated compounds by basic catalytic sites which are presented as hydrocarbon precursors to HZSM-5 catalyst. However, among MgO, CaO and FCC catalyst, CaO with HZSM-5 proved to be the best combination with 30% more aromatic yield compared to HZSM-5 alone (Zhang, Zheng, et al., 2014). In many other studies, the use of calcium oxide combination to zeolite has been supported by researchers evincing the maximum bio-oil yield, aromatics hydrocarbons and minimum production of undesired oxygenates in comparison to HZSM-5 or metal oxide alone (Liu et al., 2016; Wang, Zhong, et al., 2017; Zhang et al., 2017b).

As found in previous literature, use of mesoporous catalyst in combination to microporous has gained remarkable recognition. However, comparison of basic Magnesium oxide and Calcium oxide in conjunction to acidic zeolite catalyst making dual catalytic stage beds, especially in co-pyrolysis of SCB and PS blend as feedstock has not been reported yet. Therefore, this study aims to investigate the potential and determine the optimal mass ratio of HZSM-5:CaO and HZSM-5:MgO for co-pyrolytic oil upgradation and to analyze physicochemical characteristics of selected pyrolysis product oil.

1.2 Problem Statement

Globally depleting natural fuel reserves where world’s 79% of the energy requirements is being met by the fossil fuels, has directed the researchers to develop sustainable means of energy conversion (Gollakota et al., 2016). In this regard, utilizing renewable energy source, like biomass in the energy production by pyrolysis, is highly recommended process. Biomass is considered the only renewable resource that can be converted into several types of fuels. In combination to waste-to-energy converter, pyrolysis can be used as feedstock recycling technique for hydrocarbon waste such as wide variety of plastics for cracking them into hydrocarbon oil, gases and char (Chen et al., 2014).

However, pyrolytic-oil direct applications are limited due to 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 hydrocarbon yield has encouraged the use of mesoporous (2-50nm) catalyst with effective deoxygenation and deacidification ability, in combination to zeolite. This study aims at analyzing the combined acid HZSM-5 and basic CaO and MgO (mesoporous) catalytic impact on pyrolysis liquid oil production and its upgradation.

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

Chapter 2

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 hydrocarbons (Kositkanawuth et al., 2014).

2.2 Pyrolysis products and applications

2.2.1 Oil

Pyrolysis oil which is the complex mixture of hydrocarbon 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. Greatest advantage of bio-oil compared to standard fossil fuel is that flame from pyrolysis oil combustion is longer and harmful gas emissions is less than burning heavy oil in boilers except for particulate level (Jahirul et al., 2014). 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 hydrocarbon fuel, it is still a preferable fuel (Gollakota et al., 2016; Jahirul et al., 2014).It can also be processed to extract out methanol and Fischer-Tropsch like transportation fuels, via synthesis gas process. Besides being highly efficient energy producing fuel than hog oil or black liquor, high value-chemicals can be extracted from pyrolysis oil such as resins, fertilizers, adhesives, sugar, acetic acid, chemicals for food flavoring and industrial applications (Jahirul et al., 2014).

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. For e.g. activated char of different plastics and waste tire has shown to adsorb 3.59-2.22mg/g of methylene blue dye from wastewater (Miandad et al., 2016)
- 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 hydrocarbons. It is reported that hydrocarbon cracking occurring at elevated temperature encourages H_2 formation, carbon monoxide and carbon dioxide are produced from the decomposition of partially oxygenated organic species, and light HC generation from reformation of tar and high molecular weight hydrocarbons 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 i.e. Fisher-Tropsch from syngas and hydrogen production for NH_3 synthesis. 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 Wet and Dry Pyrolysis

Pyrolysis that is the thermal decomposition of biomass carried in an inert environment, if taken place in the presence of water or subcritical liquid is termed as Wet pyrolysis or Hydrothermal carbonization. Hydrous pyrolysis converts the organic feedstock into hydro-char keeping autogenous pressure (2-10MPa) and moderate temperature(180-350°C) at the lower zone of liquification process (He et al., 2013; Libra et al., 2011) HTC has certain advantages over dry pyrolysis such as(Shah, 2014; Sun et al., 2014):

- Eliminate the need for energy-intensive drying process of material before or after decomposition
- It gives higher solid yield and liquid with more water soluble organic species and nutrients, it is due to the fact that HTC is operated at lower temperature compared to slow pyrolysis where temperature may be set up to 600°C
- Hydro-char can be used for various applications like soil amelioration as a fertilizer or carbon sequester and innovative materials. Hydro-char being more acidic than bio-char has more nutrient value
- Hydro-char consist of less carbon and higher oxygen that makes up greater Hydrogen/Carbon and Oxygen/Carbon ratios, making it better to adsorb water-like contaminants especially after secondary oxidation.

It has been researched that sewage sludge conversion to hydro-char makes more attractive fuel in terms of higher fuel ratio i.e. FC/VM, decreased Sulphur and nitrogen content, and results in more stable and less vehement combustion. The study demonstrated decrease in volatile matter with increased HTC time, which marked to increase fuel ratio by 0.16 following 10h of carbonization. Besides affecting fuel ratio, VM reduction minimizes flame instability that would otherwise causes heat loss, as in the case of dry sludge (He et al., 2013).

2.4 Classification of pyrolysis based on operating conditions

2.4.1 Slow Pyrolysis

Slow or conventional Pyrolysis is aimed for the production of gases and charcoal since thousands of years. However, the use of inert gas for sweeping has shown to increase bio-oil yield as vapors are made to escape hot zone rapidly, inhibiting further cracking of bio-oil (Wang et al., 2016). It is also termed as carbonization process (Mohammed et al., 2016). As shown in the Table 2.1 below, this type of thermal decomposition operates at low heating rates and long residence time which therefore require more energy input (Jahirul et al., 2014).

2.4.2 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).

2.4.3 Fast Pyrolysis

Fast and flash pyrolysis both are aimed for higher liquid and gas production (Aysu et al., 2014). Short vapor residence time and rapid condensation of volatiles in fast process can produce up to 80% bio-oil yield. Compared to other energy production processes, on a small scale it may have low capital cost with relatively high energy efficiency (Jahirul et al., 2014).

2.4.4 Flash Pyrolysis

Flash or ultra-fast decomposition occurs at extremely high heating rate with rapid devolatilization. It is the advanced and modified form of fast pyrolysis with similar products distribution (Singhania et al., 2018). For better yields, particle size of feedstock must be smaller compared to other processes as it is characterized by very high temperature and low residence time (Dauenhauer, 2010).

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)

2.5 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. It is found that at reduced temperature pyrolytic-oil consist of the derivative species of the functional groups existing in feedstock. These compounds are cracked down into more stable species when the final pyrolysis temperature is increased. Usually carbon containing compounds increases and oxygenate compounds are reduced by enhanced dehydration and decarboxylation, in the oil at high temperature of pyrolysis (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 1.25mm has shown to favor high volatile production due to uniform and rapid heat flow.

For different types of pyrolyzer applied, literature has generalized the recommended particle size of biomass to be used, such as less than 2mm for fluidized bed, less than 6mm for circulating bed reactor and less than 200mm for rotating cone. Best fit size would provide appropriate inter and intra particle heat transfer, with uniform thermal energy conduction that would rapidly achieve the particle’s activation energy for biomass decomposition (Akhtar et al., 2012; Garba, 2017; Park et al., 2012).

A study on upgradation of prairie cordgrass pyrolysis oil via two stage fixed bed reactors, kept the biomass mean particle size of 0.73mm. It reported that such small particle size distribution presents greater surface area with least heat diffusion resistance, therefore providing better heat transfer during the reaction (Cheng et al., 2015). Further feedstock size impact on product yields of biomass pyrolysis in a fixed bed reactor was analyzed by another researcher. The study was made by varying particle size in between 0.15 to 0.85mm, keeping all other parameters constant. Maximum conversion of 73.85% and liquid yield of 45.02% was found with $0.15<D_p>0.224$mm. However, further increase in size led to decreased oil/gas yield but higher char formation. Such results were due to (Aysu et al., 2014);

- High thermal gradient i.e. from particles inner low temperature to outside surface higher temperature
- Cell wall is destroyed during grinding and thus releases metallic inorganic species, this inhibits secondary reactions inside the cell which otherwise lowers the liquid yield

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

However, it has been stated in literature that heating rate in fast pyrolysis has higher impact on liquid yield compared to slow pyrolysis (Aysu et al., 2014).

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 commonly applied as it is cheaply available. However, using steam shows some advantages over other gases such as enhanced heat transfer, 30-45% coke reduction, and increased bio-oil yield with higher polar compounds selectivity. Though for liquid production, steam is more preferable compared to N_2, it adds up oxygen contents in the oil therefore deteriorating product quality. On the other hand, quenching with hydrogen gas has demonstrated to significantly suppress char formation whereas liquid or gas quality in not affected (Akhtar et al., 2012; 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). A research on slow pyrolysis optimized the liquid yield by varying sweeping gas flow rate from 100 to 300cm^3/min. It was observed that liquid production increased by 1.85% when flow rate was raised from 100 to 200cm^3/min, however further increase led to decrease in yield by 4.31% due to incomplete condensation either due to poor cooling or rapid leaving of vapors (Aysu et al., 2014). However, it is stated that with adequate quenching of vapors like using dry ice, instant removal of pyrolysis vapors by high flow rate of sweeping gas, liquid yield can be optimized (González et al., 2011).

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). As pyrolysis reaction time depends on the reactors configuration and rate of heat conduction from heating element to the feedstock in reactor. So it may change with reactor dimensions and power of heating element of the system (Miandad et al., 2016).

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 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. As discussed below each reactor has its own features, mode of operation, product yielding capacity, pros and cons of its application (Jahirul et al., 2014).

2.6.1 Batch and semi-batch reactor

As the name indicates, batch process is carried out in a closed system with one-time reactant addition and products driven out only after the completion of reaction. To achieve greater conversion, reaction time can be easily increased by leaving the feedstock for longer period of time. Pyrolysis in such reactors is carried out in between 300-800°C with best controlled operating parameters yielding high liquid product (Zhang et al., 2017b).

Some of the drawbacks associated with batch reactor usage are product variations for every batch process, increased labor cost and its infeasibility for large scale application (Zhang et al., 2017b). Hence, continuous system for pyrolysis is recommended as is energy-saving in terms of operation, gives consistent end-products of the process and avoid labor fatigue of recurring unit charge with feedstock and products (Al-Salem et al., 2017). Though semi-batch reactor comes with the modification to allow partial reactant addition over time, it still does not make it suitable for large scale production and overcome high operating cost (Zhang et al., 2017b).

2.6.2 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).

2.6.3 Fluidized Bed Reactor

Fluidized bed reactors work on continuous feeding, have external heating system, well-controlled condensation and filtration units prior to products exit, that all appeals to its industrial and research application (Al-Salem et al., 2017). Its bed comprises of a fluid-solid mixture that gives high contact area per unit volume of bed, and relative velocity between solid and fluid. Such reactors are used in fast pyrolysis due to its rapid heat transfer ability, fine control of reaction conditions including vapor residence time. Classifying further, bubbling fluidized beds have shown high quality oil yield up to 75% weight of dry biomass being fed. On the other hand, circulating bed reactors owing to its short residence time and high gas velocity produces bio-oil with high char content (Jahirul et al., 2014).

2.6.4 Ablative Reactor

This reactor uses the mechanical pressure to contract the biomass against reactor’s hot wall, making the particles to melt and evaporating residual oil as vapors from its surface. This reactor application gives the advantage of using much larger sized biomass particles hence saving up energy for excessive grinding. However, ablative reactor is little complicated in design because of incorporation of mechanical system involved. Two types of reactors used for ablative pyrolysis are

- Vortex reactor
- Rotating plate Reactor

Vortex ablative pyrolysis uses stream of inert gas carrying biomass particles and hit the biomass on heated reactor wall at high centrifugal force and velocity. It can be used to carry out fast pyrolysis and have showed the liquid yield of 65%. While latter classified ablative reactor does not require inert gas medium rather feedstock is pressed against hot rotating plate with enough pressure and heat transfer to initiate pyrolysis reaction (Jahirul et al., 2014).

2.6.5 Vacuum Reactor

This type of reactors comprises of a metal belt conveyor to transfer feedstock into heated vacuum zone. Applied for slow pyrolysis, its capital and operational cost is high with much mechanical complexities in the operation (Jahirul et al., 2014).

2.6.6 Rotating Cone Reactor

Working on the same principle as fluidized bed reactor, rotating cone also follows the vigorous mixing of feedstock and hot inert material together, to effectively transfer heat among the biomass particles. However, it uses mechanical process to mix the biomass-inert particles blend, rather than using gas flow as in fluidized bed reactor (Jahirul et al., 2014).

2.6.7 Pyros Reactor

It is applied in a cyclonic reactor along with gas filter which separate out particles from the hot gas stream for producing bio-oil with minimum solid content. Pyros reactor decomposes the biomass at temperature of 450-500°C and keeps the gas residence time low (0.5-1sec) which inhibit secondary cracking. Together with the advantage of its compact structure and reduced cost, it has shown to produce bio-oil up to 75% (Jahirul et al., 2014).

2.6.8 Auger Reactor

It consists of a hot cylindrical shaped tube with an inert environment where feedstock particles are pushed into, using augers. This way biomass reaches the temperature up to 800°C for decomposition to take place, forming desired product vapors (Jahirul et al., 2014).

2.6.9 Plasma Reactor

Such reactors are made of vitreous silica tube and copper electrodes positioned in such a way to create plasma. Though plasma reactors consume a lot of energy increasing operational expense, they give some benefits over typical conventional pyrolysis reactors. Very high temperature and energy density favors fast pyrolysis which minimizes slow process problems such as increased tar and reduced syngas production (Jahirul et al., 2014).

2.6.10 Microwave Reactor

Recently microwave reactor usage has gained considerable research focus for pyrolysis process which implies the advanced mechanism of heat transfer to the waste biomass material via microwave-absorbent bed. Such bed is the mixture of biomass and microwave absorbent materials e.g. carbon particles which is adequately heated up to reach desired pyrolysis temperature upon microwave radiation absorption. Required temperature which initiate pyrolysis process, is achieved when microwave radiation ranging 1mm to 1m wavelength with the frequency of 0.3 to 300GHz is applied. Its application possesses certain advantages over conventional reactors such as (Garba, 2017; Jahirul et al., 2014; Sharuddin et al., 2016)

- High heating rate and effective heat transfer
- High production rate particularly syngas with increased chemical reactivity which lowers the production of undesirable products
- Less production cost

- Ensure exponential heating with direct energy supply to the absorbent bed thus saving time and energy in spite of heating up the whole reactor

2.6.11 Solar Reactor

Solar reactors are composed of quartz tube with opaque walls, which focuses solar radiations on the fed material that raises reactor's temperature to as high as greater than 700°C, favoring thermal decomposition of the feedstock. Main advantages of using such reactors include maximum amount of feedstock being decomposed and rapid on and off period of the system (Jahirul et al., 2014).

2.7 Type of feedstock

2.7.1 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. Moreover, biomass is the only known renewable energy source that can be processed to various valuable fuels such as solid char residue, syngas, liquid oil. 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 In various studies, it has been confirmed that bio-oil is the product of cellulose decomposition, while char residue is derived from lignin, present in feedstock (Jahirul et al., 2014).

For catalytic pyrolysis, biomass with more lignin should be opted for phenolic intermediate compounds can be derived from aromatic groups present in lignin, which are then easily converted to aromatic and aliphatic HC under the catalyst action. Also low ash content in feedstock is preferable for pyrolysis under catalytic effect because ash enhances the deactivation process of catalyst and produce undesirable acid compounds (Yildiz et al., 2016).

Furthermore, 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 aqueous phase in liquid yield (Jahirul et al., 2014). It is observed that nearly all of the initial moisture content comes out in aqueous phase of liquid yield. Moreover, moisture content increases the energy requirement for drying the feedstock and optimized pyrolysis temperature. However, minimum level of moisture must be present in biomass which act as reactant for biomass components and heat transfer medium that enhances the decomposition process (Akhtar et al., 2012). Product quality also depends on the ultimate composition of feedstock such as high oxygen content like in woody biomass yields oil with low calorific value (Abnisa et al., 2014).

It has also been found in a study that biomass with less nitrogen and mineral contents are favorable for increasing gas and bio-oil yield (Jahirul et al., 2014).It is due to the fact that during primary and secondary decomposition, inorganic species promotes charring and dehydration reactions. Presence of alkali metals like K, Ca and Na in feed material have also exhibited its catalytic effect in cracking of high molecular weight compounds, reducing tar yield. However, mineral matter can be minimized by washing of biomass with hot or cold water and acid which is a useful pretreatment leading to increment of liquid oil yield. Hot water is known to remove some main components of mineral content, while acid washing eliminate basic or acid soluble compounds present in biomass (Akhtar et al., 2012). Other pretreatment technologies include dry and wet torrefaction of biomass. Dry torrefied biomass is obtained at thermal conditions of 200-300°C in an inert environment producing solid biomass with following characteristics (Zheng et al., 2015);

- Low water content and hydrophobic in nature
- Increased energy density
- Highly grinded form

Wet torrefaction, as the name indicates is done using compressed boiling water, which perturbs the biomass structure, and then further decomposition is carried out of resulting intermediate solid product. Dry torrefaction is known to produce oil with better stability and composition carrying less water content and other undesirable organic acids, whereas later hydrothermal pretreatment is efficacious for later breakdown of cellulose by hydrolysis (Zheng et al., 2015).

2.7.2 Municipal Solid Waste

MSW 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).Plastics in the developing countries like Pakistan, makes up 12% of solid waste out of which only 1% is gone through mechanical recycling (Hoornweg et al., 2012). They are the product of crude oil processing, and so possess high amount of Hydrogen and carbon, encouraging its use as a higher value hydrocarbon feedstock for pyrolysis. All types of plastics have been found to consist of high volatile matter, which makes them produce significant amount of liquid oil product with a good calorific value. Moreover, solid residue of the pyrolysis of municipal plastic waste using red mud as a catalyst, exhibited the presence of valuable inorganic such as glass, metals along with char product. Such inorganic materials can be later on extracted for recycling process and char be applied for various useful processes (Adrados et al., 2012).

However, using Polyvinyl chloride as a feedstock is avoided as it possesses 57% chlorine content which not only give chlorinated HC in the product, deteriorating oil quality but also produces corrosive and harmful HCl (Abnisa et al., 2014).

2.8 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 HV, viscosity and PH. It is composed of a number of oxygenated compounds varying from low molecular weight like water (18g/mol) to high molecular weight oligomers (up to 5000g/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%), LHV of about 17MJ/kg, 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.

2.9 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).

2.9.1 Hydro-treating

HDT enhances the bio-oil quality, keeping boiling range unaffected via number of different processes i.e. hydrogenation, hydro-deoxygenation, hydrogenolysis and other cracking and deoxygenation reactions (Ma et al., 2015; Xiu et al., 2012). Generally, hydro-treating needs mild operating conditions but it produces low liquid yield with higher solid residue, which causes coke deposition on catalyst, and tar accumulation, may clog the reactor.

Hydrogenation, particularly adds up hydrogen content in the bio-oil as higher the hydrogen, better the quality of petroleum product is. It converts saturated olefins/aromatics into naphthalene by removing Nitrogen, Oxygen and Sulphur in the form of ammonia, water and Hydrogen sulphide. However, hydrogenation with simultaneous cracking under high pressure (100-2000 Psi) and temperature >350°C is termed as hydro-cracking which is also known to improve bio-oil quality (Xiu et al., 2012). Along with cracking reactions that promotes isomerization, aromatic hydrocarbon and coke production, pre-treating reactions are also the part of hydro-cracking which includes the elimination of N, S, O, halide and R-M compounds (Ma et al., 2015).

Hydro-deoxygenation specifically involves the modification of condensed liquid product using catalyst in terms of oxygen removal in the form of water and retaining carbon containing products (Liu et al., 2014; Yildiz et al., 2016). Conventionally it is accomplished using sulphide catalyst typically CoMo or NiMo at the temperature of 250-450°C with H_2 pressure as high as up to 30MPa. Though HDO has got a lot of attention as it has proven to significantly convert low-grade pyrolysis oil to upgraded hydrocarbon fuel, this process has certain limitations in its large scale applications because the catalyst addition and high pressure demand makes the method complex and costly. Nevertheless, HDO being carried out at atmospheric pressure using gas phase is economically viable as it can be incorporated with pyrolysis unit (Abnisa et al., 2014; Liu et al., 2014).

2.9.2 Steam reforming

At atmospheric pressure and under the conditions of high temperature i.e. 800-900°C, this process takes place in fluidized or fixed bed reactors (Garba, 2017). By this, low molecular oxygenate compounds present in pyrolysis vapors are reformed to produce hydrogen. Similar to HDO, though bio-oil quality is enhanced by conversion of oxygenates to desirable products but steam reforming is unable to increase the carbon yield of bio-oil up to the range of gasoline or diesel products (Liu et al., 2014). Moreover it is a complicated process, requiring fully developed reactors (Xiu et al., 2012).

2.9.3 Esterification

Solvent addition in the bio-oil that are polar in nature and has HHV e.g. CH_3OH, C_2H_6O, $C_5H_4O_2$ have demonstrated to homogenize the oil giving desirable characteristics including enhanced volatility and miscibility with diesel. Present in various organic and inorganic compounds, organic acids conversion to corresponding esters ameliorate the quality of bio oil. It has been found that after esterification acid number, water contents, aging rate and viscosity is lowered while chemical stability, heating value together with corrosion is increased. Such quality upgradation can also be achieved by adding solvent after pyrolysis (Garba, 2017; Xiu et al., 2012).

2.9.4 Emulsification

Using surfactants bio-oil can be emulsified with hydrocarbon fuels that provides one of the simplest way to improve oil quality. Though emulsification has provided the application of pyrolysis oil in diesel engine with better ignition property, still corrosion, heating value and cetane number need further approach for improvement. In addition to this, design and production requires high energy input (Xiu et al., 2012).

2.9.5 Supercritical extraction

This involves using supercritical fluids to extract out the compounds which do not dissolve in liquid or gaseous state of solvent, encouraging gasification and liquefaction reactions. This has shown to increase calorific value of oil and reduce its viscosity. Out of other fluids and organic solvents, water has been widely used in hydrothermal processing, however using it for biomass liquefaction presents some disadvantages;

- Decreased yield of water-insoluble compounds
- Produces highly viscous oil with increased oxygen content

Therefore, organic solvents such as C_4H_9OH, $(CH_3)_2CO$, C_2H_6O, CH_3OH, C_3H_8O and some other have been employed to improve oil quality. The production of such SCFs is environment friendly and performed at lower temperature, but still application of such organic solvents is not cost-effective on large scale and hence has promoted researchers to look for cheap organic solvent as substitute (Xiu et al., 2012).

2.9.6 Co-pyrolysis

Another process that has shown to up-grade the bio-oil along with its improved yield is co-pyrolysis. 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. Though there comes the idea of blending oil from two different feedstock resulting from separate pyrolysis, however unstable mixture formation that causes phase separation due to different nature of both oil and high operation cost by increased energy consumption on two individual processes, does not appreciate the idea of mixing two oils. Not only this, co-feeding biomass with higher H/C_{eff} feedstock such as plastics is 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 notably (Abnisa et al., 2014; Kim et al., 2017). .

2.9.7 Catalytic Cracking

In general, there are two types of catalyst that are used in various industrial and chemistry research that are (Sharuddin et al., 2016);

- Homogenous which involves single phase i.e. catalyst is in the same phase as that of reactants
- Heterogeneous catalyst, involving more than one phase, which are more widely used and preferred

Most commonly used homogenous catalyst are basic NaOH and KOH in industries and $AlCl_3$ particularly in pyrolysis of solid waste, however use of such catalyst have some major drawbacks due to which solid heterogeneous catalyst synthesis and usage is preferred. As homogenous catalyst is consumed by the end of reaction so its separation from the products is not only difficult but requires high cost equipment that would separates the catalyst producing lot of wastewater. Therefore, such catalyst is not feasible to be regenerated or reused. On the contrary, heterogeneous catalyst like metal oxides, supported catalyst, metal complexes can be easily separated out from the end products without being consumed or adding up impurities. As well as these catalysts can endure extreme operating conditions of the process, such as temperature and pressure up to 1300°C and 35MPa respectively (Al-Salem et al., 2017; Zabeti et al., 2009).

Catalyst addition in the pyrolysis process can improve bio-oil quality via off-line cracking or on-line catalytic cracking i.e. 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

In-situ mode of operation where there is direct physical contact of feedstock with the catalyst is found to perform remarkably better in terms of oil quality upgradation as compared to ex-situ mode. However, this mode of catalyst placement is still not highly recommended as it may permanently deactivate the catalyst because of mineral accumulation, consuming increased amount of cracking catalyst in the reaction (Veses et al., 2014; Yildiz et al., 2016).

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).

2.9.7.1 Types of Catalyst

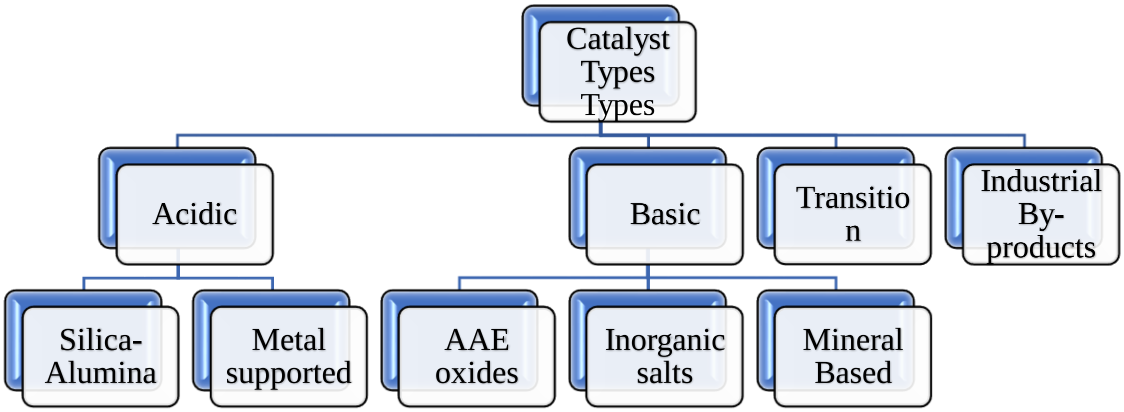


Figure 2.1 Catalyst types

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 hydrocarbon 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, HMOR, HY, H-mordenite, ZSM-5 and other inexpensive materials like sepiolite, bentonite 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 0.54-0.56nm 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

As such physical structure, textural configuration like pore size which affects selectivity of MAH and chemical properties i.e. acid sites, influencing cracking ability of catalyst (López et al., 2011; Zhang et al., 2018), makes HZSM-5 to favor fragmentation of biomass in pyrolysis with enhanced deoxygenation and dehydration reactions, aromatization, dealkylation and other reactions pathways which results into rapid production rate of upgraded bio-oil.

However, the most important property of catalyst that is acidity, especially Bronsted acidity which can be tuned by Si/Al ratio must be well adjusted to maximize the cracking of oxygenated compounds. Generally, lower the Si/Al ratio more will be acid sites available for catalytic reactions but too low ratio may lead to dealuminization which makes catalyst structure unstable (Garba, 2017; Liu et al., 2014).

Other than HZSM-5, Al-MCM-41 molecular sieve of M41S family has grabbed attention in various studies to be used as catalyst for not only upgrading bio-oil with more aromatics but to overcome the issue of rapid deactivation, increased water production, gas formation instead of organic yield, and undesirable PAH as experienced in micropore HZSM-5 usage. Its larger pore size up to 10nm in hexagonal structure configuration provides a sufficient surface area around greater than 1000m^2/g.

In addition to this, studies have demonstrated that mesoporous catalyst exhibit stronger acid sites. This accommodates larger oxygenated species molecule, promotes cracking, decarbonylation and deoxygenation of such heavy molecules in to HC, and lighter oxygenates. Another mesoporous catalyst with comparatively better hydrothermal and thermal stability due to wall thickness in between 3-9nm and pore size up to 50nm has gained due attention as well (Garba, 2017; Lappas et al., 2012).

ii. Metal supported catalyst

By metal modification, bi-functional property i.e. both Lewis and Bronsted base-acid sites are introduced to the catalyst used as support. Transition metals Ni and Co, doped on ZSM-5 catalyst support has shown minimized activity for water formation while enhances aromatic HC and phenol production in bio-oil. Such transition metals develop active sites on HZSM-5 promoting steam reforming and has demonstrated to decrease Bronsted acidity but increase Lewis acid sites. Similarly, Magnesium and Boron metals can also be applied for adjusting acidity of HZSM-5 for optimized catalytic activity. AAE metals also when dispersed on support like Silica-alumina make up efficient heterogeneous catalyst as metal ions are strong electron donor, which particularly favors double bond migration of olefins. Moreover, metals supported on char can be synthesized to be used as an effective catalyst in high temperature pyrolysis (Garba, 2017; Liu et al., 2014).

b. Base catalyst

Most of the acid catalyst due to their micro-pore structure experiences fast deactivation due to coke deposition, which not only results into lower yields of oil but also ends up with undesirable PAHs product. Though using mesoporous or macrospore acidic catalyst such drawbacks can be overcome, hydrothermal instability and higher synthesize cost of such catalyst has brought into attention the application of 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).

a. 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 (without any catalyst). 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).

ii. Mineral based materials

Natural low-cost clay minerals such as Calcite (CaO), Dolomite (CaO.MgO), Colemanite, Sodium perborate monohydrate are used as heterogeneous catalyst to improve oil quality to fuel grade. They have exhibited to (Garba, 2017);

- Significantly remove acidic compounds and oxygenates by dehydration reactions from oil
- Fixing CO_2 containing compounds in pyrolysis oil by adsorbing it from gaseous product
- Increasing bio-oil HV and affecting phenolic compounds content in liquid yield

A study was made to compare the effect of different natural catalyst Kaolin, Mabisan, bentonite clay and dolomite on the liquid yield obtained from waste plastic pyrolysis. The presence of Silicon and Aluminum content in catalyst, which increases cracking ability, was higher in Mabian and Kaolin clay i.e. 15-25% of both elements. Hence, both these natural clay demonstrated highest liquid yield >65% compared to other catalyst (Kyaw et al., 2015).

iii. Inorganic salts

Essential inorganic elements like potassium, sodium, calcium, magnesium, phosphorus present in biomass demonstrate catalytic cracking characteristics in pyrolysis. Usually these inorganic species increases char and solid residue production (particularly K and Ca) while lowers the gas formation, though potassium is known to increase decarbonylation and decarboxylation reactions as well (Liu et al., 2014). Salts in the form of chlorides, sulphates and bicarbonates have known to affect chemical composition in pyrolysis end product also influencing pyrolysis temperature. Moreover, such salts if impregnated on biomass particles results into secondary reaction inhibition during thermal decomposition. All metal salts significantly increase CO_2 and char production, however alkali metal chloride salts NaCl, KCl exhibit higher production rate compared to alkaline earth metals salts $MgCl_2$, $CaCl_2$. Hence such salts containing reactive compounds act as catalyst for bio-oil upgradation in pyrolysis (Garba, 2017).

c. Industrial by-product

Red mud is the most tested and researched by-product of industrial process to be used as catalyst in pyrolysis. It is alkaline in nature with pH 12-13, comprising of different metal oxides including Fe_2O_3, Al_2O_3, TiO_2, Na_2O, Al_2O_3. It is a waste product of Bayer process during which pure Aluminum metal is extracted from its bauxite ore. It has been studied to (Garba, 2017);

- Increase deoxygenation reactions that leads to lower oxygen content
- Elevating HV of pyrolysis oil with increased H/C ratio

- Decrease acidity and viscosity of bio-oil

A research study pyrolyzed plastic waste in the presence of red mud, which concluded that addition of such low cost waste material as catalyst favors the production of less viscous, lighter bio-oil with increased aromatic HC. Also it upgraded the oil quality with the desirable BTEX compounds instead of styrene formation (Adrados et al., 2012).

d. Transition metal oxides

Various transition metals such as nickel, zirconium, zinc, Titanium, Iron-3, cerium and Manganese, in oxide form have been employed in catalytic pyrolysis of biomass. It has been found that Titanium oxide, Iron-3 oxide, Nickel oxide and zinc oxide lowers the liquid or organic product yield but enhance the production of gases, H_20 and solid residue. Few metal oxides have been tested as effective support catalyst e.g. Aluminum oxide and Titanium oxide, as well as mixture of different oxides have demonstrated higher catalytic activity than a single catalyst alone (Liu et al., 2014).

A research study investigated the effect of various metal oxides on the pyrolysis of sewage sludge. Comparing TiO_2, Fe_2O_3, and ZnO it was noticed that Titanium lowered the final temperature of pyrolysis by 50°C, therefore decreasing reaction time while other two elevated the end temperature by 235 and 103°C thereby increasing the pyrolysis time. Moreover, Fe_2O_3, and ZnO gave higher char yield which inferred that both catalyst prevents fragmentation of organic compounds present in sludge (Shao et al., 2010).

2.9.7.2 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 0.52-0.59nm 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). Moreover, another study researched on to create mesoporous intra-particle arrangement within microporous ZSM-5, treatment with sodium hydroxide was found effective, that resulted in enhanced aromatics with least coke formation compared to pure microporous catalyst.

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 gives 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, 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 VM vapors into lighter HC fuel precursors which then undergoes acidic catalyst sites to be converted into desirable MAH, demonstrated in the Figure 2.2 below (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). One of the important consideration while using two different catalysts is its placement that significantly affects product quality. A notable work carried out in 2014 compared different mode of catalyst placement when using combination of HZSM-5 and CaO catalyst, it was noted that maximum yield in terms of aromatic HC was as in the order of (1) Dual stage catalytic mode > (2) Feedstock+CaO mixed and ex-situ bed of HZSM-5 > (3) in-situ mixture of both catalyst +feedstock > (4) catalytic single bed of CaO+ZSM mixture (Zhang, Zheng, et al., 2014).

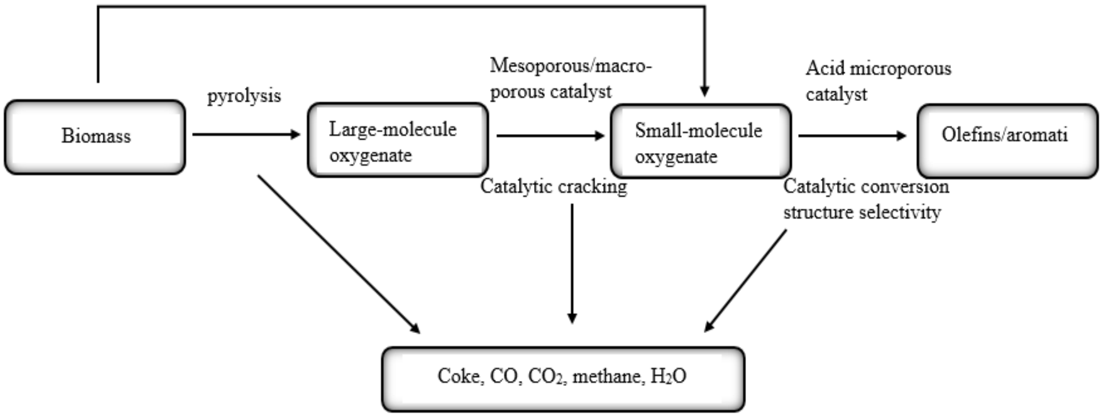


Figure 2.2 Pyrolytic vapors cracking over mixed catalyst

2.9.7.3 Reaction Conditions using catalyst

Many operating reaction parameters like temperature, catalyst to feedstock ratio, feedstock blend ratio, residence time affects the product distribution and composition as well as coke formation during catalytic pyrolysis (Liu et al., 2014). Some of these factors are discussed below in detail;

a. Reaction Temperature

Generally, coke deposition on catalyst active sites is irreversible at higher temperature, decreasing the number of Bronsted sites more critically than Lewis acid sites. To avoid dealumination i.e. irreversible damage to catalyst which occurs at 450°C for decomposition of high moisture content feedstock, temperature below 400°C has been recommended in the previous literature (Liu et al., 2014).

A latest study researched on the temperature impact on different catalyst i.e. silica gel, AC and 5A molecular sieve. It was noticed that silica gel and activated carbon exhibited contrary behavior with rising temperature compared to molecular sieve. Silica gel, AC decreased its catalytic cracking ability former due to hydrophobic site creation, which causes weak adsorption of polar compounds and later catalyst owing to carbon deposition. Whereas molecular sieve yielded highest biomass conversion at elevated temperature of 700°C (silica gel, AC maximum conversion at 450°C) possibly due to enhanced thermal vibration within feedstock molecules and crystalline catalyst structure, which ultimately lead to higher diffusion of biomass molecules into the micropores of 5A molecular sieve catalyst (González et al., 2011).

Another research carried out using HZSM-5 catalyst in ex-situ mode inferred that higher catalytic temperature i.e. 350°C compared to 200°C gave less coke yield (0.02% vs 3.16%) owing to the fact that thermal cracking of long chain carbon waxes and phenols to lighter compounds is promoted under increased temperature (Duan et al., 2017).

Reaction temperature in the presence of catalyst affects not only the bio-oil yield but also the selectivity of aromatic and other organic compounds in the product composition. Pyrolysis conducted using bi-functional HZSM-5/MgO demonstrated that varying temperature in between 450-600°C caused decrement in phenolic compounds by 19.8% as temperature was raised from 450 to 500°C but then further increase in temperature i.e. up to 600°C elevated phenols production by 58.4% whereas aromatic production showed exact opposite trend (Fan, Chen, et al., 2017).

b. Effective Hydrogen Index

It is one of the crucial parameter that affects catalyst performance in pyrolysis, can be expressed as eq. (1)

$$\frac{\mathrm{H}}{\mathrm{C}}_{\mathrm{eff}} = \frac{\mathrm{H-2O-3N-2S}}{\mathrm{C}} \qquad (1)$$

effective H/C depends on the molar ratio of elemental carbon, oxygen, nitrogen and Sulphur present in the biomass (Wang, Zhang, et al., 2017). In general, lower EHI of feedstock is observed to cause more rapid and significant coke deposition on catalyst making it deactivated (Liu et al., 2014). Various researchers have reported that feedstock with effective hydrogen to carbon ratio of less than 1 makes the catalyst esp. HZSM-5 vulnerable to deactivation and therefore inhibits its cracking ability for conversion of waste biomass to valuable HC yield (Ding, Zhong, et al., 2018; Liu et al., 2016; Wang, Zhong, et al., 2017; Zhang et al., 2018). To circumvent this issue while using low EHI feedstock, co-pyrolysis with higher H/C biomass such as plastics (H/C 1-2) is preferred that serves as hydrogen donor. In a study it was demonstrated that increasing LDPE loading in feedstock blend more olefins production enhanced aromatics but lessens phenols formation, moreover high EHI of resulting blend promoted the conversion of lignin-derived oxygenates into HC (Fan, Chen, et al., 2017). Effect of this parameter on product yield was also studied in 2017 by varying EHI in between 0.19-1.86 using high H/C feedstock i.e. waste lubricating oil different loading. It was observed higher proportion of waste lubricating oil promoted aromatic production that may be attributed due to decreased formation of PAH which otherwise cause destruction of catalyst cracking ability (Wang, Zhang, et al., 2017). Similarly another researcher concluded in its study that keeping H/C in between 0.4-1 with HZSM-5/CaO catalyst during co-pyrolysis produced higher petrochemicals yield than decomposing individual biomass separately (Zhang et al., 2017b).

c. Feedstock to Catalyst ratio

Usually increased catalyst loading leads to higher vapor residence time which converts active species into lighter HC compounds and increased secondary cracking results in lower oil and char yield whereas gas formation increases (Fan, Chen, et al., 2017). A research study demonstrated that increased loading of dual catalyst HZSM-5/USY enhanced the aromatic yield with increasing ratio up to 1:6, however further increment showed decreased production. It was attributed to the fact (Zhang et al., 2018);

- Before optimum ratio, insufficient catalyst amount led some of the oxygenated vapors to pass through without converting to HC
- At even higher loading, all carbon compounds got settled on the catalyst surface, owing to less diffusion into the pores, hence forming coke and favoring all HC conversion to lighter HC compounds

Another researcher, listed in the Table 2.2, studied the effect of varied feedstock to catalyst ratio in xylan pyrolysis over dual catalytic stage bed. As mentioned increased catalyst loading to 1:6, favored the production of aromatic by 32.48% and reduction in oxygenates formation by 44.72%. However, it was discerned that rate of HC production was lower than catalyst increment in loading, as well as PAH formation was enhanced at higher loading, hence catalyst loading must be optimized to appropriate level (Ding, Zhong, et al., 2018). On the contrary, a study summarized in the Table 2.2 below, exhibited decreased oil production from 55.8 to 32% with increasing ratio of 1:0 to 1:2, while gas yield and coke formation increased by 13.9% and 9.9% respectively (Williams et al., 2003).

d. Metal oxide to HZSM-5 ratio

Co-pyrolysis of lignin and LDPE with HZSM-5 in conjunction to MgO (1:1) exhibited comparable aromatic production with minimum char formation than implying either catalyst alone. However, it is to be inferred that zeolite 3D porous structure is more favorable for benzene like compound formation which attributed to decreased HC yield with increasing MgO : HZSM-5 ratio. Compared to MgO alone, with increasing MgO loading in dual catalyst combination it is discerned that bio-oil yield increment by 8.3% is because of the fact that MgO favors alkylation of phenols that adds weight in the oil (Fan, Chen, et al., 2017). Another research results as reported in the Table 2.2 depicts that dual catalyst of HZSM-5 and CaO positively not only influenced the olefin and aromatic selectivity in product oil but also suppressed the undesirable product formation such as acids, PAH to 2% (Wang, Zhong, et al., 2017). It is known that CaO converts the acidic compounds into ketones, which are then converted into aromatics by HZSM-5. It was clearly noticed in a study when decreased CaO loading in dual bed led to increased acid content in oil with lower ketones and vice versa (Ding, Zhong, et al., 2018). Similarly another study found that PAH selectivity was reduced with higher Magnesium oxide loading in combination to HZSM-5 which is one of the desirable objective as PAH are considered to be carcinogenic and precursor to coke deposition that ultimately leads to catalyst deactivation (Wang, Zhang, et al., 2017).

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
Lignin & LDPE	HZSM-5, MgO	In-situ	450, 500, 550, 600	1.16	1:1	1:1	1:1	32% bio-oil at 500°C but optimum 550°C gave 30.2% oil with less char and increased gas yield than 500°C	(Fan, Chen, et al., 2017)
			550	0.02, 0.66, 0.84, 1.16, 1.44, 1.87	1:0 , 3:1 ,2:1, 1:1, 1:2, 0:1	1:1	1:1	35.9% bio-oil at 3:1 (0.66) but optimum at 1:2 (1.44) with 28.6% oil and phenol and aromatization completely	
			550	1.16	1:1	1:1	0:1 , 1:2 , 1:1, 2:1, 1:0	1:1 min char but 8.3% less bio-oil than max obtained by HZSM only, converting all oxygenates and HC to aromatics	
			550	1.16	1:1	1:0, 2:1, 1:1, 1:2	1:1	1:1 with max 30.2% , converting oxygenates and HC to aromatics completely	
Bamboo residue & waste tyre	HZSM-5, CaO	Ex-situ dual stage	600	0.62, 0.57, 0.51	2:3, 1:1, 3:2	-	-	At 1:1 (0.57) max 67% HC, min content of VACs i.e. 17% and undesired products(UP) of 5.9%	(Wang, Zhong, et al., 2017)
							1:0, 0:1, 4:1, 3:2, 2:3, 1:4	At 2:3 max 73.6% HC and 9.5% alcohol, min 2% UPs	

Table 3.2 Acidic HZSM-5 and basic catalyst combined use in pyrolysis (continued)

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	0.02, 0.48, 0.72, 1, 1.24, 1.42, 1.31	1:0, 4:1, 2:1, 1:1, 1:2, 1:4, 0:1		1:1	At 1:2 (1.24) max vio-oil 31.44% and aromatic yield of 29.33% 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)

Table 4.2 Acidic HZSM-5 and basic catalyst combined use in pyrolysis (continued)

Feedstock	**Catalyst**	**Mode of Operation**	**Temp °C**	**EHI**	**FBR**	**F:C**	**O:HZSM-5**	**Result**	**Ref**
			600	0.67	4:1		4:1, 1:1, 1:4, 3:2, 2:3, 0:1	2:3 yielded max 39% aromatics, 21% olefins+alkanes, min ketones 3.7% and 2%acids	
			600	0.19, 0.67, 1.22, 1.37, 1.64, 1.86	1:0, 4:1, 3:2, 2:3, 1:4,0:1		2:3	2:3 (1.37) with max 70% aromatics	
Ageratina adenophora **&** **Kerogen**	HZSM-5, CaO	in-situ	450, 500, 550, 600, 650	0.02	1:0	1:2	1:3	At 550°C max petrochemicals 21.9%, min carbon yield of unidentified oxygenates(UO) 3.5%	(Zhang et al., 2017b)
			550	0.02	1:0		0:1, 4:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4, 0:1	1:3 max aromatics 12.6%, olefins 8.8% and total petrochemicals 21.9%	
			450, 500, 550, 600, 650	1.31	0:1		1:3	At 650°C max total petrochemicals of 54.8%	

Table 5.2 Acidic HZSM-5 and basic catalyst combined use in pyrolysis (continued)

Feedstock	Catalyst	Mode of Operation	Temp °C	EHI	FBR	F:C	O:HZSM-5	Result	Ref
			650	1.31	0:1		0:1, 4:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4, 0:1	At 1:3 max petrochemical of 54.8% and min UO 2.1%	
			450, 500, 550, 600, 650, 700, 750	1	0.325:0.675		1:3	Highest petrochemical of 47.5% at 600°C	
			600	0.02, 0.4, 0.6, 0.8, 1, 1.2, 1.31	-			at EHI of 0.4-1, petrochemical yield of copyrolysis is higher than pyrolysis of individual biomass at their optimal 550 and 650°C temp	
Pine sawdust	HZSM-5, CaO, MgO, FCC	in-situ	600			1:6	0:2 - 3:1	ZSM:CaO:MgO optimal of 2:1:0.22	(Zhang, Zheng, et al., 2014)
							1:2 with Ca and 0.22:2 with Mg	Total 30% more aromatic yield with Ca compared to ZSM alone, giving highest yield	

Table 6.2 Acidic HZSM-5 and basic catalyst combined use in pyrolysis (continued)

Feedstock	Catalyst	Mode of Operation	Temp °C	EHI	FBR	F:C	O:HZSM-5	Result	Ref
							1:2 CaO	highest yield of indene and other HC with dual stage, then CaO in-situ +ZSM bed gives the yield more than pure ZSM	
Bio-oil mode compound & Ethanol	HZSM-5, Ga_2O_3		400, 2MPa	-			0:1, 1:19, 1:9, 3:17, 1:4	3:17 i.e. 20% oxide loading yielded max 39.2% wt oil phase with 71% monoaromatics	(Wang et al., 2014)
			300, 350, 400, 450				3:20	At 400°C all reactants completely converted, with ~95% aromatics HC in liquid	
Hemi-cellulose & LLDPE	HZSM-5, CaO	ex-situ dual stage	600	0	1:0	1:2	1:0, 2:1, 1:1, 1:2, 0:1	highest yield of aromtaics(31.66%), min yield of PAHs and max BTXE (benxene toluene, xylene, ethyl benzene)at 1:2 with respect to single HZSM-5	(Ding, Zhong, et al., 2018)
				0	1:0	1:2, 1:4, 1:6	1:2	yield of aromatics, aliphatics and PAHs ↑ with ↑catalyst loading whereas oxygenated compounds↓	
				0, 0.75, 1.27, 1.65, 1.94	1:0, 3:1. 1:1, 1:3, 0:1	1:2	1:2	highest yield of aromtaics 40% with 1:1 (EHI 1.27)	

Table 7.2 Acidic HZSM-5 and basic catalyst combined use in pyrolysis (continued)

Feedstock	Catalyst	Mode of Operation	Temp °C	EHI	FBR	F:C	O:HZSM-5	Result	Ref
Corn stover + LDPE	HZSM-5. CeO_2	ex-situ dual stage	600		1:0	1:6	1:5, 2:1, 1:1, 1:2, 5:1	Max yield of HC (aromatics+aliphatic) of 85.53% and min oxygentaed 14.47% at 1:2	(Ding, He, et al., 2018)
					1:1	1:6, 1:4, 1:2	1:2	1:4 yields almost same quantity and selectivity of HC as with 1:6 and ~3% oxygenates only	
					5:1, 2:1, 1:1, 1:2, 1:5	1:4	1:2	1:2 (0.7 EHI) optimum for 95.48% HC, 78.02% MAH selectivity	

Chapter 3

Materials and methods

3.1 Feedstock

3.1.1 Preparation

SCB was obtained from local sugar mills industry, Pakistan. It was sun-dried for 8-10h to reduce moisture content, to the extent that uniform grinding is achieved using a mechanical grinder. To achieve even more consistent particle size distribution, bagasse sample was sieved to obtain particle size between 1.8 to 0.4mm. Generally, smaller particle size allows better heat transfer/distribution during pyrolysis, however, too small particle size offers higher resistance to sweeping gas, making pressure drop of the reactor higher. The recommended particle size for maximum liquid yield is 0.4 to 1.8 mm (Onay et al., 2004). Prior to use in pyrolysis, SCB sample was oven dried at 105°C for 24h to reduce its moisture content to less than 10% by weight. Commercial PS polymer grains (1-2mm diameter) purchased from a local Petrochemical industry in Pakistan were used as received in pyrolysis reaction.

Figure 3.1 SCB and PS used in the reaction

3.1.2 Characterization

A thorough characterization of both SCB and PS samples, used in co-pyrolysis, was performed. For elemental composition of the feedstock, both samples were finely ground to obtain particles size ≤0.6mm before the ultimate analysis was performed by CHN analyzer (Perkin Elmer 2400) according to ASTM D5291-96, while oxygen content was calculated by difference. The proximate analysis was performed following the ASTM D3172-07 standard procedure. Furthermore, component analysis of SCB was done according to the method mentioned in literature (Ahmed et al., 2018) To determine calorific value of raw material, Isoperibal Bomb Calorimeter (Parr Model 6200) was used as per the standard procedure ASTM D5865.

Thermoanalytical measurements comprising of thermal decomposition trend of pure SCB, PS and 1:1 PS:SCB blend were made by TGA (Mettler Toledo). Almost 13.9, 6.1 and 11.4mg of PS, SCB and SCB:PS blend with a particle size ≤1mm were placed in Al_2O_3 crucible to ascertain uniform heating and kinetic control during the degradation process. Providing the inert conditions with Nitrogen flow rate of 50ml/min, sample was then heated from ambient temperature to 600°C at a ramp of 20°C/min.

3.2 Catalyst

3.2.1 Preparation

All three catalyst used were commercially available analytical lab grade chemicals. Alkaline earth metal oxides CaO and MgO used in the study, were in granular form with average particle size of 2mm (Park et al., 2010). However, HZSM-5 was in cylindrical extrudate form with 1mm diameter and 5mm in length as reported to be used earlier (Williams et al., 2003). All catalysts were calcined at 600°C in a muffle furnace for 5h and stored in desiccator before being used in co-pyrolysis process.

Figure 3.2 CaO, MgO and HZSM-5 catalyst

3.2.2 Characterization

The textural properties of the calcined catalyst samples were determined by surface area analyzer (Micromeritics Gemini Vll, 2390T), using nitrogen adsorption isotherm obtained at -196°C (Stefanidis et al., 2011). Prior to analysis, samples were degassed at 300°C for 2h in vacuum. Specific surface area was measured by multipoint Brunauer, Emmett and Teller (BET) and Langmuir equations respectively (Wang et al., 2017b). Barret, Joyner and Halenda (BJH) method was employed to get the pore size distribution (Stefanidis et al., 2011) whereas total pore volume was obtained by the amount of

Nitrogen adsorbed at relative pressure (p/p_o) of 0.95. Moreover, micropore volume was determined by using T-plot method (Zhang et al., 2017), whereas mesopore volume was calculated by eq. 2

$$V_{meso} = V_{Total} - V_{micro} \quad (2)$$

Chemical composition of each of the catalysts was analyzed using XRF spectrometer (JSM-3202M of Jeol), equipped with X-ray tube (excitation source) of Rhodium anode and Silicon Lithium Si(Li) detector as reported previously (Kumar et al., 2014).

3.3 Experimental Set-up

3.3.1 Fixed bed reactor and Accessories

The pyrolysis system consisted of two reactors installed in series, followed by a condenser unit. The schematic diagram of apparatus is shown as figure 3.3. The fixed-bed thermal reactor (R1), internal diameter and height of 10.4 cm and 50.8cm respectively) and catalytic reactor (R2) with smaller working volume (internal diameter and height of 4.2cm and 36cm respectively) were constructed of 316 stainless steel (SS). Condenser unit was formed by helical copper coil with tube internal diameter and total length of 0.6cm and 75cm respectively, submerged in a cooling mixture of ice and NaCl salt, maintaining -2 to-5°C temperature. Feedstock was fed into R1, encapsulated in a stainless steel crucible supported by SS gauze and ceramic wool, in such a way that biomass placement was at the center of the reactor. Likewise, catalyst bed was maintained in the middle part of R2, supported by SS mesh at the bottom.

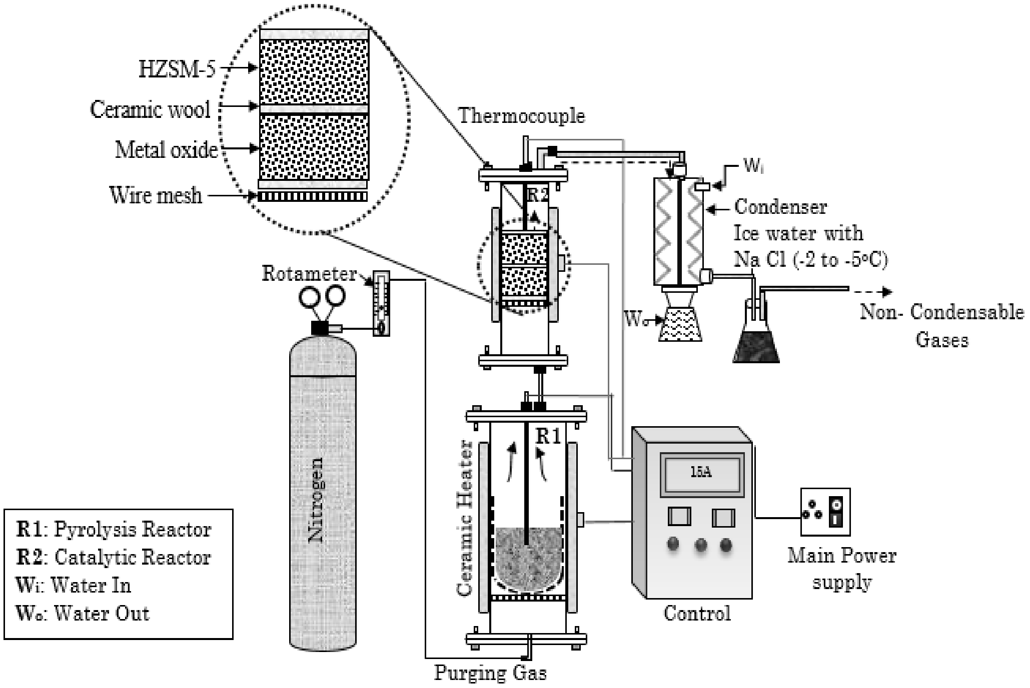


Figure 3.3 Schematic diagram of apparatus

Both the reactors were heated with ceramic band electric heater tightly wound around the external wall. Temperature of the two reactors was controlled separately with K-type thermocouples connected to PID controllers. To prevent heat loss to the surrounding, system was fully insulated using 12mm thick ceramic fiber blanket wrapped by fiber glass tape, both possessing low thermal conductivity and capable of sustaining high temperature (~800°C).

3.3.2 Operating Procedure and Conditions

A 100g of feedstock blend with 1:1 mass ratio of PS:SCB was prepared and loaded in R1. Keeping feedstock:catalyst mass ratio of 1:1 throughout the experimental study, total of 100g of catalyst was loaded each time in R2. As demonstrated in the Figure 3.3, the vapors coming from R1, first passed through macro/mesoporous CaO/MgO catalyst granules and then through microporous HZSM-5, both catalysts separated by a layer of ceramic wool. Moreover, to keep the catalyst bed intact, wool was placed at top and bottom of the bed as well. However, for comparative purpose, a non-catalytic experiment run was conducted in which catalyst was replaced by glass beads to observe the extent of thermal cracking only. All the connections of the system were then tightly closed and to create inert environment, purging with a Nitrogen was carried out at a flow rate of 800cm^3/min for 30mins. After purging and before start of the actual experimental run, N_2 flow rate was adjusted to 50cm^3/min (sweeping gas) for the rest of the experiment. The temperature of R2 was first raised to the set value of 550°C and then heating of R1started from room temperature at a ramp of 35°C/min until the set temperature of 500°C was achieved where it was then kept constant for 30 minutes (at least) or until no more condensate was collected in a flask. After each trial, system was left to cool for 2h, before the solid residue and spent catalyst was removed, and thereafter whole system was cleaned with acetone and dried prior to next run.

The experimentation was carried out in two series, first with CaO/HZSM-5 dual catalytic bed and second with Magnesium oxide/HZSM-5 at different loading as presented in the Table 3.1. To ascertain the reproducibility, each reaction was carried out twice.

Table 8.1 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

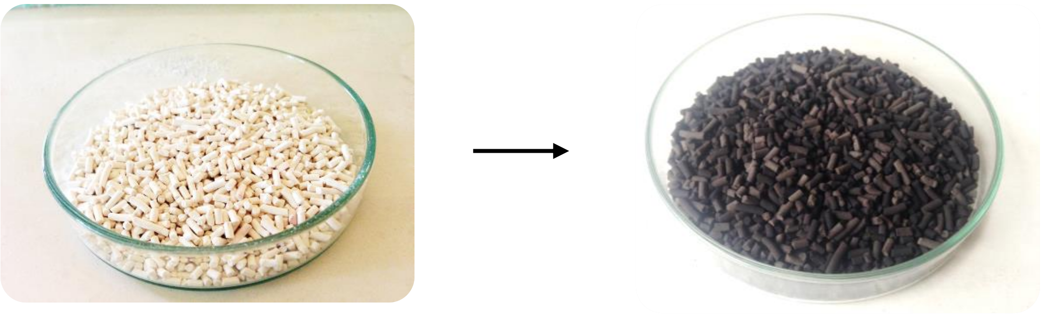
3.3.3 Products collection

Four of the products of each trial were collected as follows;

- Condensed liquid in the flask was weighed in grams and reported as Liquid-oil yield.
- When the system was cooled, it was dissembled and solid residue (Char), left in the pyrolysis reactor was recovered and determined gravimetrically.
- Spent catalyst was removed from the catalytic reactor and amount of coke deposited was calculated as change in mass of catalyst before and after the trial.
- Then gas yield was found by the calculating the difference of Bio-oil, char and coke from the initial feedstock weight i.e. 100g.

Liquid yield

Char



Fresh catalyst

Spent catalyst

Figure 3.4 Products collected

3.3.4 Oil phase separation

The oil produced consisted of two layers; the aqueous and organic layers. It was filled in 50ml aliquots and centrifuged at 1500 rpm for 30 minutes (Veses et al., 2014). It was observed to form distinct upper organic phase (OP) and bottom, aqueous phase (AP) layers after centrifugation, and were separated by decantation. Furthermore, OP was passed through anhydrous sodium sulphate bed via filtration to completely remove any remaining moisture content (Ahmed et al., 2018), prior to its physicochemical characterization. AP left was measured gravimetrically and so OP yield was calculated by eq. (3)

$$= \text{Total oil yield} - \text{AP} \qquad (3)$$

3.4 Analytical techniques for product oil

The optimum dual catalyst loading of both HZSM-5:CaO and HZSM-5:MgO was identified after analyzing the distribution and selectivity of organic compounds present in the product oil using GC-MS. Combination yielding highest MAH, lowest undesirable products like PAH and acids was then further analyzed to determine other parameters through respective analytical techniques. Moreover, product oil of non-catalytic trial was also characterized for comparison.

3.4.1 Chemical analysis

Major chemical components present in the OP samples were determined by GC-MS (Shimadzu QP2020), equipped with DB-5 ms capillary column of 30m length × 0.25mm

I.D ×0.25µm film thickness. 1µL of sample volume was injected with the split ratio of 1:107. High purity Helium was employed as carrier gas with a column flow of 1.47ml/min. At first the initial temperature of 30°C was kept constant for 2min and then with an increment of 8°C/min final oven temperature of 290°C was achieved where it was given the hold time of 20 minutes. The temperature of injector and interface were kept constant at 260°C and 295°C respectively. MS was operated with electron ionization being set at 70eV along with mass to charge ratio (m/z) in the range of 35-500 (Ding et al., 2018b).

By comparing with National Institute of Science and Technology (NIST) mass spectral library, the obtained chromatograms of organic species were identified. Relative content of each compound was measured by semi-quantitative method by calculating the chromatographic peak area.

3.4.2 Physical analysis

Physical characteristics that were analyzed to further compare the OP quality with petroleum fuel characteristics included pour point, flash point, kinematic viscosity, density, and HHV. Pour point was measured as per the ASTM D97 using cloud and pour point test equipment by Koehler Instrument Company. Flash point was determined according to ASTM D93 using Pensky-Martens closed-cup flash tester (K16000. Koehler Instrument Company). A redwood viscometer was employed to measure the kinematic viscosity at 40°C with the test method of IP 70. Similarly, a simple test was performed by weighing 5ml of oil sample, collected in a graduated syringe to get the oil density by dividing weighed mass over 5ml volume (Veses et al., 2014) . Additionally, to get the energy content Isoperibal Bomb Calorimeter (Parr Model 6200) was used as per the ASTM D240, HHV of the oil content was measured.

Chapter 4

Result and discussion

4.1 Feedstock analysis

The characteristics of both SCB and PS, used as feedstock in the co-pyrolysis, are given in the Table 4.1. Since PS contains mainly carbon and hydrogen, it possesses greater calorific value than SCB that constitutes less elemental carbon, hydrogen and relatively more oxygen content (López et al., 2011; Özsin et al., 2017). Approximate molecular formulae (dry basis) of both PS and SCB are $C_{7.53}H_{8.6}O_{0.04}N_{0.029}S_{0.001}$ and $C_{4.23}H_{5.7}O_{2.68}N_{0.039}S_{0.002}$ respectively. As depicted in the formulae, SCB has lower H/C_{eff} ratio of 0.05, making it hydrogen-deficient reactant in pyrolysis process. On the other hand, PS has H/C_{eff} of 1.12 that makes it a hydrogen source in cop-pyrolysis and when co-fed with biomass, it increases the overall Effective Hydrogen Index (EHI) of feedstock that tune up catalyst performance, favoring enhanced hydrocarbon (HC) and less coke yield (Zhang et al., 2017; Zhang et al., 2014a).

The proximate analysis showed presence of high volatile matter in both feedstock, which shows higher potential of yielding significant amount of liquid oil. However, SCB contains substantial amount of ash and fixed carbon which is likely to affect burning rate of the product oil, leading to poor combustion and inefficient energy conversion with increased char formation (Ahmed et al., 2018; Zhang et al., 2014a). Besides, presence of moisture in SCB promotes AP production in liquid yield via dehydration reactions during pyrolysis. Fiber content analysis of biomass revealed that SCB has high lignocellulose (62.7wt.%) which makes it a good potential feedstock for fuel production (Özsin et al., 2017; Rabiu et al., 2017).

Table 9.1 Physicochemical and energy properties of feedstock

	SCB	**PS**
Ultimate Analysis (wt.%)		
C	50.8	90.4
H	5.7	8.6
O	42.9	0.6
N	0.5	0.4
EHI*	0.1	1.1
Heating Value (MJ/Kg)	17.8	42.3
Proximate Analysis (wt.%)		
Volatile Matter	75.0	96.9
Fixed Carbon	16.6	0.7
Ash	3.5	0.6
Moisture	4.9	-
Compositional Analysis (wt.%)		
Cellulose	42.5	
Hemicellulose	26.4	
Lignin	19.7	
Extractives	11.3	
Bulk Density (kg/m^3)	125.0	610.0

*calculated by $\frac{\mathrm{H-2O-3N-2S}}{C}$

Thermal degradation curve for SCB, PS and the 1:1 blend (both observed and calculated) are shown in Figure 4.1. Decomposition of SCB occurred in three stages. In first stage (100 to 200°C), around 7% weight loss occurred, which is associated with removal of water and extractive breakdown. The second stage commenced at around 220°C and continued up to 380°C with a further weight loss of around 55%. This decomposition is attributed to hemicellulose and cellulose degradation. The third and final SCB degradation stage (400 to 480°C) is attributed to lignin decomposition, made further weight loss of 12%. However, residue of about 20% of initial dry mass accounts for fixed carbon that is converted to char and ash at the end of pyrolysis reaction (Asadullah et al., 2007; Dewangan et al., 2016; Ghorbannezhad et al., 2018).

On the other hand, PS being more thermally stable, started to decompose at 370°C exhibiting steep mass loss curve up to 500°C with a weight loss of 96.9%. However, with further increment of temperature, no significant weight loss was visualized making the residue leftover of 1.3% at the end. When the mixture of PS and SCB was subjected to TGA analysis, the maximum weight loss was observed to shift to higher temperature zone i.e. above 290°C (as compared to that for SCB sample alone) and continued up to 500°C. Furthermore, to analyze if the synergetic effect existed between these two feedstock, a theoretical weight loss curve as calculated by the Eq. (4) is depicted in the Figure 2 for comparison with the experimental curve.

$$w_0 = w_{SCB}.x + w_{PS}.y \qquad (4)$$

Where, w_{SCB} is weight loss of SCB, w_{PS} is the weight loss of PS under same temperature and x, y are the respective mass fractions of SCB and PS in the mixture respectively. It is to be noted that the blend decomposition followed the calculated curve up to 320°C and then deviated. After 440°C, the blend curve followed the PS decomposition curve hinting that the biomass had been degraded by 440°C. Hence, in between 320°C to 440°C, likelihood of noticeable synergistic effect was observed during co-pyrolysis. Moreover, 50% reduction in residue in experimental co-pyrolysis as compared to theoretical one, also hints about synergistic effects taking place for the blend, which may be explained by potential enhanced depolymerization, and volatilization owing to interaction between SCB and PS degraded components (Aboulkas et al., 2009). TGA results revealed that the optimum temperature for co-pyrolysis of SCB and PS is 500°C beyond which no substantial mass loss is observed (Li et al., 2012).

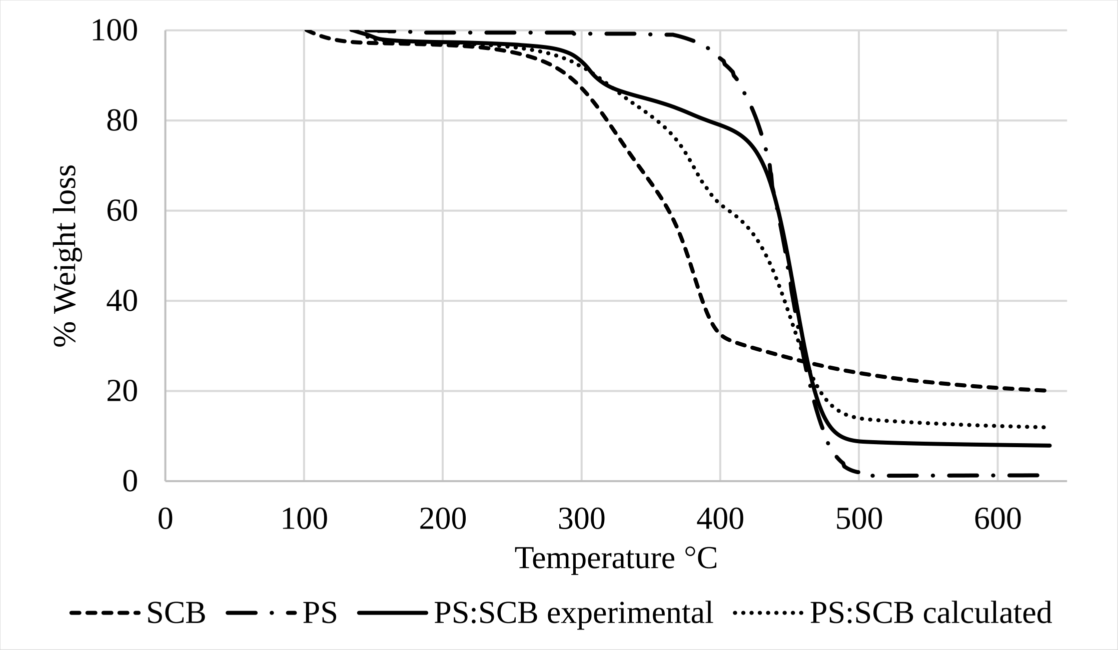


Figure 4.1 TGA profile of SCB, PS and the blend

4.2 Catalyst analysis

Table 4.2 shows the XRF analysis of the catalysts, identifying compounds that were detected in noticeable quantities.

Table 4.2 XRF analysis of the catalysts used in the study

Catalyst	**Chemical Content wt.%**				
	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3
HZSM-5	97.0	3.0			
MgO	1.2	-	98.1	0.2	0.5
CaO	3.0	-	-	96.4	0.6

Morphological properties of the three catalysts are presented in the Table 4.3 (BET parameters of catalyst). HZSM-5 exhibited highest BET surface area, possessing higher micropore volume. However, no micropores were detected in both CaO and MgO samples, making their textural structure highly mesoporous.

Table 4.3 BET parameters of catalyst

Catalyst	**BJH Average Pore size nm**	**Surface Area m^2/g**		**Porosity cm^3/g**		
		BET	Langmuir	V_{total}	V_{meso}	V_{micro}
HZSM-5	1.5	283.2	403.3	0.105	0.045	0.061
MgO	28.5	32.7	60.6	0.233	0.233	0.000
CaO	44.7	11.1	14.1	0.124	0.124	0.000

4.3 Catalyst influence on product distribution

The yield, in terms of weight percentage of feedstock converted to product, with varied dual catalyst bed ratios and non-catalytic blank is depicted in Figure 4.2. Highest relative bio-oil production of 51wt.% (with least amount of AP) was achieved without any catalyst addition. In the presence of catalyst, the OP production decreased with a simultaneous increment of AP yield, which is in accordance with the yield trend found earlier (Stefanidis et al., 2011) while investigating the effect of acidic and basic catalyst on woody biomass pyrolytic end-products distribution. Similarly, studying pine wood chips pyrolysis in fluidized bed reactor using three different catalysts MgO, CaO, and HZSM-5 at catalyst:feedstock of 1:1 also exhibited a similar results of decreased oil yield and elevated gas formation compared to non-catalytic trial (Mahadevan et al., 2015).

Once used in the catalytic process, the white color of all three catalysts was changed to dark grey, depicting coke deposition. Variation in coke yield (Figure 4.2) among three catalysts can be explained by mesoporous structure for MgO and CaO that favors higher coke production compared to microporous HZSM-5. However, CaO being more basic in nature compared to MgO, got higher coke deposition (0.13g/gCaO) than MgO (0.048g/gMgO), on average (Kabir et al., 2017; Lin et al., 2018). Therefore, the slight variation in solid products' yield in all catalytic runs compared to non-catalytic run, is explained by this difference in coke formation and deposition on different catalysts. Since ex-situ mode of catalyst placement does not influence the feedstock decomposition process in pyrolysis reactor, so constant char yield (about 17wt.% on average) was found for all variations in experiment (Stefanidis et al., 2011).

Overall, an increase in gaseous products is noted in catalytic runs which can be explained by multiple possible factors. Enhanced gaseous yield can be attributed to increased secondary reactions owing to higher gas residence time in the presence of catalyst (due to its higher porosity) at higher temperature. Moreover, CaO and MgO addition as catalyst may also lead to higher gaseous yield as reacting with water, these catalysts form basic aqueous which potentially promotes H_2 formation leading to higher gas yield (Kuan et al., 2013). Another potential factor influencing incondensable vapors production using basic catalyst is the enhanced ketonization that promotes CO_2 formation (Ding et al., 2018a). On the other hand, HZSM-5 favors decarbonylation reactions, leading to increased gas yield with expected higher CO fraction (Stefanidis et al., 2011). The reasons for higher gaseous products in catalytic pyrolysis can be analyzed with higher level of certainty if the gaseous composition is also investigated.

For bi-functional HZSM-5:CaO, as seen in Figure 4.2, with an increasing ratio, oil yield decreased from 46wt.% (CaO only) to 37.5wt.% (HZSM-5:CaO of 3:1) and then increased to 44wt.% with HZSM-5 alone. The increased share of CaO in the catalyst leading to increased oil production is in agreement with the findings of previous study conducted to investigate pine wood pyrolysis in a fluidized bed reactor, which showed oil yield increment of 10.1wt% with increased CaO:feedstock ratio from 0 to 5 (Lin et al., 2010). One probable reason for decreased oil yield with higher HZSM-5 loading in the bi-functional catalyst is its 3-D mesoporous structure and acidic nature that favors secondary cracking reactions, yielding less oil product (Kabir et al., 2017).

In series 2 (Figure 4.2), bio-oil production with HZSM-5:MgO decreased dramatically from 44wt.% using HZSM-5 only, to 35wt.% at HZSM-5:MgO of 3:1, in the catalyst. However, with further increase in MgO loading, oil yield increased gradually up to 47wt.% (HZSM-5:MgO of 1:3). Previously, another study (Fan et al., 2017a) investigated the effect of catalytic co-pyrolysis of lignin and LDPE and reported similar oil yield trend in the presence of MgO and HZSM-5 catalyst. Higher MgO loading that lead to increased oil formation was attributed to enhanced alkylation which promotes phenols formation, thus adding up weight in bio-oil.

Hence, the dual catalyst bed of HZSM-5 with both CaO and MgO, exhibited the similar trend of decreasing oil yield with increasing HZSM-5 loading. However, HZSM-5 addition in MgO lowered the liquid yield to greater extent than CaO i.e. by 24.7% compared to 18.48% with the addition of 0 to 75wt% HZSM-5, indicating maximal catalytic effect by MgO/HZSM-5. This indicates that metal oxide loading in bi-functional catalyst increases oil yield, however for MgO, the highest yield (47wt.%) was observed at 1:3 of HZSM-5:MgO rather than 100% MgO.

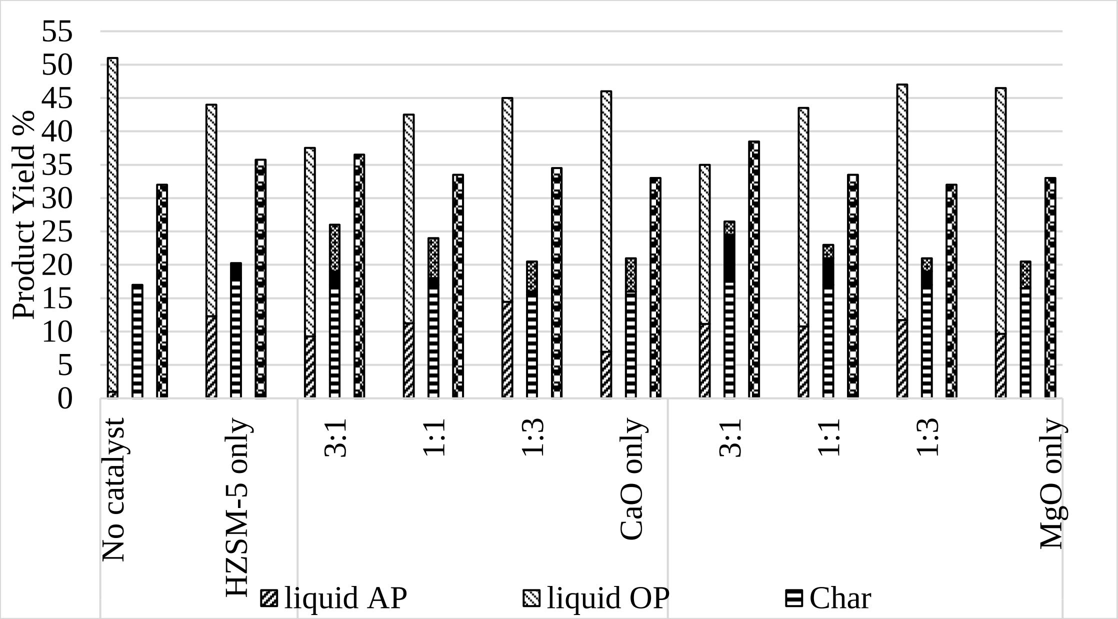


Figure 4.2 Pyrolytic end-products yield for considered combinations of catalysts

4.4 Catalyst influence on oil composition

4.4.1 GC-MS of oil

Results of the GC-MS analysis for all oil samples are presented in Table 4.4. For non-catalytic co-pyrolysis, HC compounds from PS decomposition i.e. MAH and Olefins dominate in the liquid OP composition by 80.6wt.%. Whereas, SCB-derived chemical species such as alkanes, phenols, furans, acids, ketones and other oxygenates are found with only 5.58 wt.%. This agrees with the previously reported study that PS addition inhibit the formation of compounds originating from biomass decomposition in liquid yield (Suriapparao et al., 2018). However, no new product that could have been formed by the cross-reaction between biomass and plastic intermediates were identified, as all the compounds are the result of individual pyrolysis of SCB or PS as found in previous studies (Bhattacharya et al., 2009; Li et al., 2014). It is to be noted that no styrene was formed in any of the catalytic or non-catalytic co-pyrolysis oil which may be explained by the higher residence time of pyrolytic vapors in the catalytic reactor (due to presence of catalyst/glass beads) at high temperature (550°C) that resulted in cracking and hydrogenation of styrene monomers to alpha methyl-styrene, other benzene derivatives and olefins (alkenes) (Miandad et al., 2017; Shadangi et al., 2015). Higher methyl styrene content (about 7.5wt.%) was observed in the presence of both basic catalyst, compared to that of HZSM-5 (3.8 wt.%). This is in agreement with the previously reported studies finding higher styrene yield in basic-catalytic pyrolysis as secondary cracking reactions over catalyst proceed in a similar way of depolymerization in thermal pyrolysis (Achilias et al., 2007; Tiwary et al., 2010). Among PAH, naphthalene yield was escalated by 23wt.% (MgO only), 52.9 wt.%(HZSM-5 only), and 8.24 wt.% (CaO only) compared to non-catalytic yield, which could be explained by enhanced de-alkylation and aromatization in the presence of catalyst. Furthermore, higher indene selectivity in the catalytic oil composition particularly highest in HSZM-5 alone, compared to basic catalysts is due to formation of methyl-phenyl indane, that are produced by chain scission or cyclization of hydrogenated styrene dimer, which undergoes further cracking into indene derivatives (Shah et al., 2014; Tiwary et al., 2010; Xue et al., 2017).

Furans, which are the product of holocellulose dehydration reactions (Lu et al., 2010; Mahadevan et al., 2015) , phenols derived from lignin degradation (Ahmed et al., 2018), carboxylic acids and other fatty acids like Hexadecanoic and Octadecanoic acid originating from biomass extractives (Mendes et al., 2016), were all greatly reduced by catalyst addition. MgO alone, lowered the phenolic compounds by 73.4wt.%, furans and acids each by approximately 85 wt.%. However, for CaO phenolic yield and its composition was observed to be almost same as that of non-catalytic pyrolytic oil indicating that unlike MgO or HZSM-5, to a very little decrement in yield CaO polymerized phenolic compounds to solid residue (char or coke) instead of aromatic production (Lu et al., 2010). Furthermore, CaO alone increased acidic contents of the oil to greater extent which is in contradiction to the literature where various studies have found that CaO completely eliminates acids owing to its strong basicity (Lin et al., 2018; Lu et al., 2010) . Hence, out of three catalysts, HZSM-5 has shown maximum conversion efficiency of acids, furans and phenols presenting them as hydrocarbon source for aromatic production via deoxygenation (Mendes et al., 2016).

Furthermore, MAH obtained at varied ratios of MgO/HZSM-5 and CaO/HZSM-5 catalyst was analyzed, to understand the effect of catalyst composition on MAH proportion in oil as MAH is a desirable oil component. Illustrated in Figure 4.3, with increasing HZSM-5 proportion, MAH production increased from 37wt.% (CaO only) to 50.1 wt.%(HZSM-5 only) which may be attributed to the fact that HZSM-5 pore size matches the kinetic diameter of aromatic compounds, thereby making it selective to 6-membered ring species formation (Ding et al., 2018b; Fan et al., 2017a; Zhang et al., 2018). Though at 3:1 HZSM-5:CaO combination, 8wt.% less mono-aromatic was obtained as compared to highest MAH yield, it is noteworthy that undesirable products like oxygenates (including acids, ketones) as well as PAH were 57wt.% and 18.3wt% respectively, lower than those of sole HZSM-5. Such reduction in large oxygenated compounds and subsequent increase in MAH over dual-catalyst bed is most likely attributed to pyrolytic vapors pathway from mesoporous CaO catalyst favoring conversion of heavier compounds to lighter ones, followed by further cracking to aromatics by microporous HZSM-5 bed (Liu et al., 2016).

As depicted in Figure 4.3, MAH production with MgO/HZSM-5 combination showed a fluctuating trend, however at 50% and 75% by weight addition of MgO in catalyst, apparent synergetic effect in terms of higher MAH yield was exhibited. At 75% addition of MgO, along with maximum formation of MAH (56.8wt.%,), relatively lowest PAH content (20.8wt.%) was detected in oil composition. Moreover, aliphatic HCs showed an increasing trend with increased MgO addition, suggesting pore size of MgO likely favoring olefins production whereas HZSM-5 cracking long chain HC to aromatics (Fan et al., 2017a).

On the other hand, raising MgO proportion in the catalyst reduced acids and phenols production along with higher ketones in the oil, which is consistent with the findings of other studies which attributed this to accelerated deacidification, deoxygenation and aldol condensation by basic catalyst, converting acids and carbonyl compounds into ketones. Ketonization and aromatization of these hydrocarbon precursors take place in

HZSM-5 catalytic sites which produce gasoline-like compounds (Lin et al., 2018; Wang et al., 2017a).

Therefore, dual-catalyst bed that integrates acid and basic sites is conducive for better catalytic performance, yielding improved oil quality, rather than employing either HZSM-5 or metal oxide alone in catalytic co-pyrolysis of PS and SCB. Acids that cause corrosion and rapid ageing of oil (Lu et al., 2010) , phenols which contribute to weight and increases oil viscosity (Mahadevan et al., 2015), and all other oxygenated compounds that generally lower the heating value of oil were noticeably reduced by optimal dual catalyst combination. Nevertheless, HZSM-5:MgO optimal ratio of 1:3 yielded higher selectivity of MAH (56.8wt.%) and lesser undesirable PAH (20.8)wt.% in comparison to (46wt.% MAH and 26.8wt.% PAH) selectivity obtained by optimal 1:3 CaO:HZSM-5. This implies that, considering given parameters, MgO upgraded oil composition to greater extent than CaO combined with HZSM-5.

Table 4.4 %. Peak area of chemical compounds identified by GC/MS in liquid OP

			HZSM-5:CaO				HZSM-5:MgO			
	No catalyst	HZSM-5 only	3:1	1:1	1:3	CaO only	3:1	1:1	1:3	MgO only
Monoaromatic hydrocarbon										
Benzene	10.62	27.17	28.3	25.8	24.4	19.47	25.3	33.0	26.4	20.47
Alpha-methly Styrene	9.32	3.78	3	2.24	2	7.45	1.48	4	5.23	7.42
Other Derivatives	17.48	19.17	3.19	15.3	3.38	10.04	15.7	3.7	25.1	19.08
			14.5	9	13.0		8	15.0	5	
					4			3		
Polyaromatic hydrocarbon										
Indane	0.1	1.91	1.82	2.07	2.24	0.83	0.57	0.47	0.34	1.12
Indene	3.22	9.45	9.01	8.48	10.4	6.74	10.5	4.13	8.62	6.52
Naphthalene	6.68	14.19	10.2	11.9	1	7.28	4	18.7	7.84	8.68
Fluorene	0.48	1.73	3	1.52	14.7	0.71	21.2	1	1.2	0.97
4-Phenanthrenol,	0.05		1.36	0.06	1		1	1.23	0.05	0.15
Anthracene	1.96	2.97	2.58	1.32	1.39	0.11	1.79	0.03	2.75	1.83
Phenanthrene	1	1.3	1.1	2.47	1.08	1.68	3.26	2.07	0.96	0.94
Fluoranthene	0.06	0.32	0.08	0.03	2.06	0.08	1.49	1.19	0.04	0.07
Pyrene		0.32	0.17	0.16	0.09	0.03	0.17	0.78	0.08	0.3
Chrysene			0.02	0.17	0.21		0.28	0.12	0.12	
Phenalene			0.02		0.19		0.02	0.18		
Triphenylene	0.1	0.29	0.19			0.15	0.02			0.12
							0.25			

Table 4.4 %. Peak area of chemical compounds identified by GC/MS in liquid OP (continued)

			HZSM-5:CaO				**HZSM-5:MgO**			
	No catalyst	HZSM-5 only	3:1	1:1	1:3	CaO only	3:1	1:1	1:3	MgO only
Aliphatic Hydrocarbon										
Olefins	43.15	15.17	25.64	27.05	23.72	35.03	16.17	17.39	20.2	28.88
Alkanes	0.92	0.9	1.12	1.2	0.8	4.54	1.24	1.32	0.48	1.62
Oxygenates										
Phenol	1.39	0.15	0.05	0.09	0.13	1.35	0.06	0.21	0.34	0.37
Furan	1.83	0.04	0	0	0.02	0.21	0	0.06	0.05	0.23
Hexadecanoic acid	0.11	0.03	0.01	0.09	0.03	0.66	0.01	0.04	0.04	0.04
Octadecanoic acid	0.09	0.02	0.11	0.14	0.04	0.53	0.02	0.02	0.01	0.03
Other acids	0.57	0.02	0.06		0.18	2.26	0.12	0.06	0.09	0.05
Ketones	0.51	0.23				0.33			0.03	0.69
Ether, alcohol, aldehydes, ester	0.16	0.12				0.48				0.24

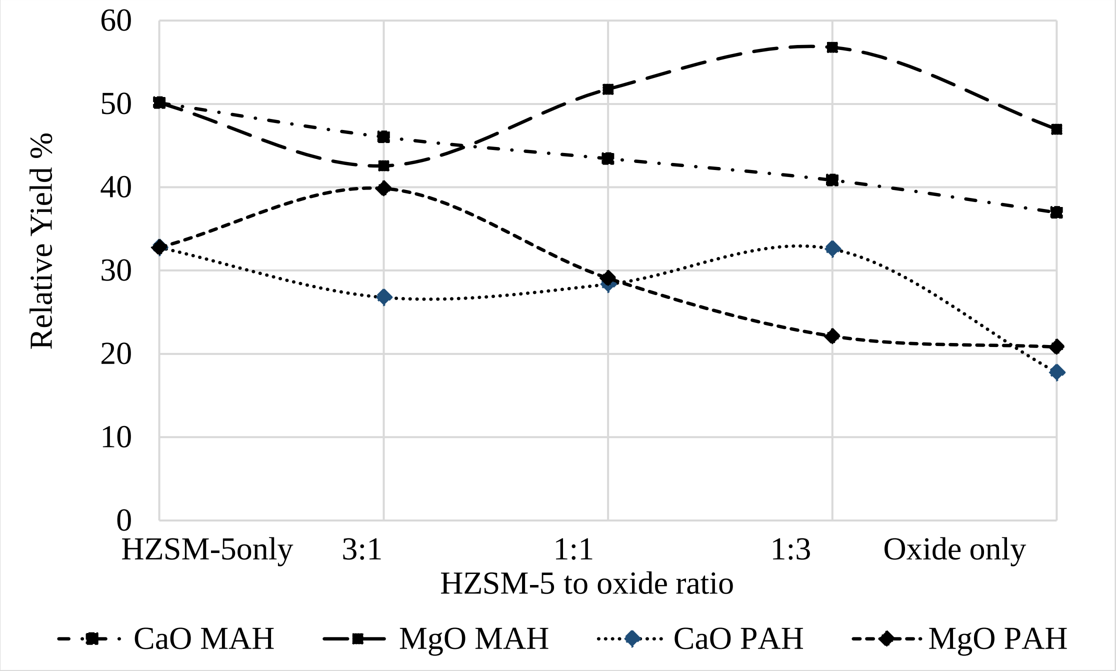


Figure 4.3 Aromatic Hydrocarbon selectivity of catalyst combinations in liquid OP

4.4.2 Physical properties of oil

Table 4.5 presents the physical characteristics of organic phase of product oil obtained by using optimal catalyst combinations (CaO:HZSM-5 of 1:3, MgO:HZSM-5 3:1) and that without use of catalyst to compare with the conventional fuel (diesel) quality. As shown in the Table 4.5, there was a little difference in pour point and flash point of catalytic and non-catalytic pyrolytic oil. Pour point that is less than -40°C presents good potential of its use in colder regions where otherwise fuel possessing higher pour point has adverse impact in engine start-up due to prolonged wax formation that likely leads to blockage of the filter and fuel system (Miandad et al., 2017; Miandad et al., 2016). Due to high volatility and contents of aromatic hydrocarbon compounds (Miandad et al., 2017), flash point of the pyrolytic oils were found to be very low, hinting about the requirements of extra safety precautions and care during handling.

Favorable changes were noted with dual-catalyst addition in terms of improved density, kinematic viscosity and calorific value, which were found to be comparable to the diesel quality. Higher kinematic viscosity is known to cause poor atomization of fuel when sprayed in combustion chamber, thereby affecting engine performance. Moreover, dense and viscous fuel exhibits resisted flow and hence adds up to pumping cost (Miandad et al., 2017; Miandad et al., 2016; Veses et al., 2015). Use of catalyst in co-pyrolysis was found to reduce kinematic viscosity by 26.3%. Though, viscosity of pyrolytic oil without any catalyst was already in the standard diesel range (of 2 to 5cSt), improvement in density with (HZSM-5:MgO) catalyst was noteworthy to upgrade the oil close to fuel characteristic value of 0.87g/cm^3. Furthermore, heating value that specify the amount of fuel required to get the target energy was raised slightly by combined use of basic catalyst and HZSM-5, close to conventional fuel specified range and hence showing its potential as an alternative transportation fuel.

Table 4.10 Physical properties of selected liquid OP

Characteristics	**No catalyst**	**CaO:HZSM-5 1:3**	**MgO:HZSM-5 3:1**	**Conventional fuel (Diesel)**
Pour Point °C	< -40	< -40	< -40	Max 18[a]
Flash point °C	23	24	24	55-60
Kinematic Viscosity at 40°C (cSt)	4.56	3.36	3.36	2-5[b]
Density at 15°C g/cm^3	0.89	0.88	0.87	0.815- 0.870
HHV MJ/kg	40.6	41.4	41.5	43.06

[a]Miandad et al.,2016, [b]Miandad et al.,2017

Chapter 5

Conclusion

The co-pyrolysis of SCB and PS at 1:1 weight ratio blend demonstrated enhanced feedstock conversion to aromatic hydrocarbons in liquid yield with application of acidic (HZSM-5) and basic (MgO/ CaO) catalysts both, used individually or in combination, as compared to the aromatic liquid yield with use of catalyst. Synergism between microporous HZSM-5 and mesoporous MgO, CaO active site promoted hydrocarbon yield and suppressed PAH and oxygenates formation. Reduction in large oxygenated compounds and subsequent increase in MAH over dual-catalyst bed could be attributed to pyrolytic vapors pathway from pyrolysis chamber to mesoporous CaO/MgO catalyst followed by microporous HZSM-5 bed. This favors the conversion of heavier compounds by CaO/MgO to lighter ones, that undergoes further cracking to aromatics by HZSM-5. Though at 1:3 CaO:HZSM-5 combination, 8wt.% less mono-aromatic was obtained as compared to highest MAH yield obtained over HZSM-5 alone, undesirable oxygenates (e.g. acids and ketones) as well as PAH were (57wt.% and 18.3wt% respectively) lower than sole HZSM-5. Nevertheless, MgO:HZSM-5 optimum ratio of 3:1 yielded higher MAHs (i.e. 56.8wt.%) and lesser PAH (i.e. 20.wt.%) in comparison to selectivity of (46.0wt.%) MAH and (26.8wt.%) PAH by optimal CaO:HZSM-5 weight ratio of 1:3. Additionally, favorable changes were noted with dual-catalyst bed of HZSM-5 with CaO and MgO in terms of improved density and calorific value, close to conventional fuel specified range and hence showed its potential as an alternative transportation fuel.

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