

Catalytic and Non-Catalytic Co-Pyrolysis of Corn Stalk and Polystyrene with a focus on Liquid Yield and Quality



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A thesis submitted in partial fulfillment of the requirements for the degree of
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I certify that this research work titled “*Catalytic and non-catalytic co pyrolysis of Corn Stalk and Polystyrene with a focus on Liquid yield and quality*” is my own work. The work has not been presented elsewhere for assessment. The material that has been used from other sources as been properly acknowledged/referred.

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ABSTRACT

In this study non-catalytic and catalytic co-pyrolysis of Corn Stalk (CS) and Polystyrene (PS) was conducted in a fixed bed reactor at 500C (selected based on TGA results) to evaluate the effect of feedstock blend ratio, catalyst to feedstock ratio (CFR) and mode of catalyst addition. CS and PS were co pyrolyzed in various proportions that is 1:0, 1:3, 1:1, 3:1, 0:1. Increasing PS in mixture showed positive synergy in case of liquid oil with maximum synergy evidenced at CS to PS ratio of 1:3. Whereas, direct comparison between in-situ and ex-situ using HZSM-5 Catalyst, under identical conditions revealed that In-situ yielded more liquid oil and mono aromatics hydrocarbon (MAH) yet less poly aromatic hydrocarbons (PAH) and acids which was attributed to difference in residence time of pyrolysis vapors. However increasing CFR in twain modes led to decrease in overall MAH and oxygenates and increase in PAH and acids. With regard to aromatics selectivity, maximum selectivity to BTEX and negligible selectivity to styrene was noticed at ex-situ CFR of 1. In comparison to non-catalytic, catalytic yield less MAH so further physical analysis of non-catalytic was carried out which elucidated liquid oil encompasses properties close to conventional fossil fuels.

Key Words: *Co-pyrolysis, Ex-situ, In-situ, HZSM-5, Catalyst to feed stock ratio, aromatic hydrocarbons*

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LIST OF ABBREVIATIONS

CS	Corn Stalk
PS	Polystyrene
BET	Brunauer, Emmett and Teller
XRD	X ray diffraction
HHV	High heating value
GC-MS	Gas chromatograph-Mass spectroscopy
CFP	Catalytic Fast Pyrolysis
CFR	Catalyst to Feedstock ratio
ZSM-5	Zeolite Socony Mobil -5
MAH	Mono aromatic hydrocarbons
NIST	National Institute of Standards and Technology
Py-GC/MS	Pyrolysis-gas chromatography/mass spectrometry
PAH	Poly-aromatic hydrocarbons
PP	Polypropylene
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
SAR	Silica to Alumina ratio
TGA	Thermogravimetric analysis
WS	Wheat Straw
XRD	X-ray diffraction

Chapter 1 INTRODUCTION

1.1 Background

Rapid escalation in population, urbanization, industrial and commercial growth and technological evolution leads to a terrific increase in world energy demand, which in turn depleting the fossil fuels, which is currently meeting 80% of the global energy demand, tremendously (Agency, 2013; Kim et al., 2015; Kim et al., 2017). According to Energy Information Administration world energy consumption will rise by 28% from 2015 to 2040. Though it is predicted that energy consumption by all the fuel sources will rise, but renewables are likely to be the fastest growing energy source, with consumption surging by an average of 2.3% per year within the era of 2015 to 2040 (Administration, 2017). This is certainly due to the fact that the masses are shifting towards renewable energy sources as conventional fossil fuels have high prices, deteriorating air quality and have high carbon intensity, i.e. amount of CO₂ released from each unit of energy produced (Iliopoulou et al., 2012).

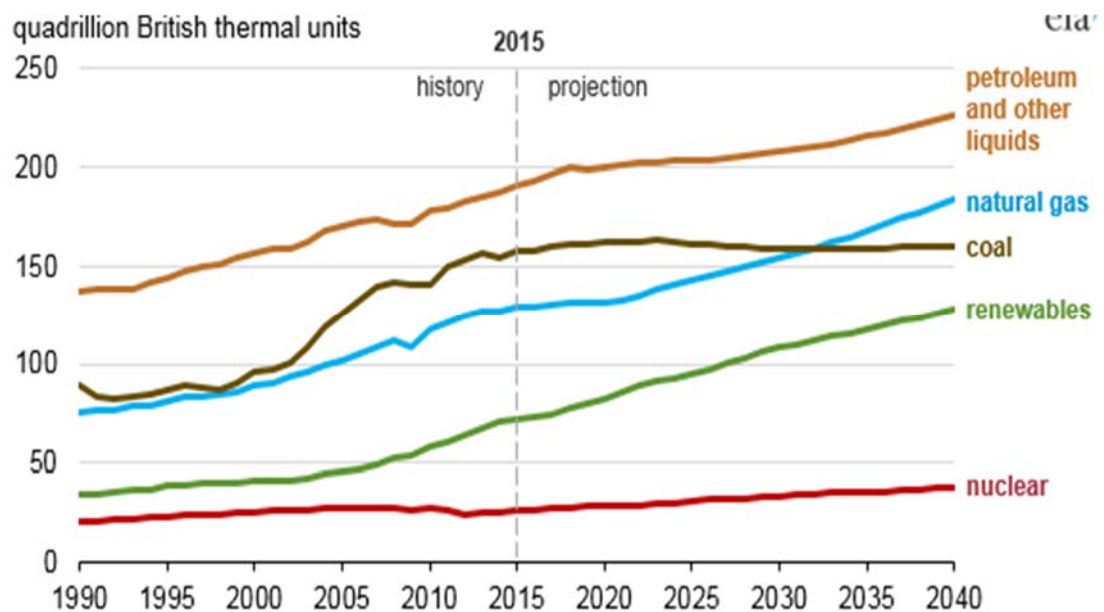


Figure 1.1.1 World Energy consumption by energy source (1990-2040)

Among renewable energy sources, biomass is a promising and emerging energy source, as it is renewable, abundant, readily available, cheap, CO₂ neutral and has the potential to contribute to a more secure energy supply (Iliopoulou et al., 2014). At present, biomass production in the world is approximately 150 billion metric tonnes per year and is the fourth largest energy source after coal, petroleum and Natural gas, and accounting 14% of the world's energy consumption Ateş et al. (2006); (El Mogahzy, 2009; Iliopoulou et al., 2012). It can be transformed to Liquid (bio-oil), solid (bio-char) and gaseous fuels through numerous conversion processes. These conversion processes are categorized into three routes Iliopoulou et al. (2012).

Table 1.1 Biomass to biofuel conversion techniques

Technique		Brief description	Principal products
Biochemical	Microbial Digestion	It involves microorganism to break down biomass components in the absence of oxygen	Methane, Carbon rich biogas
	Microbial Fermentation	It involves yeast to breakdown carbohydrate present in biomass to alcohol	Bio ethanol
Thermochemical	Gasification	Process of converting feedstock/biomass in a limited quantity of air into producer gas,	Syn gas (H ₂ , CO)
	Combustion	Burning of biomass in stoichiometric amount of air	Hot combustion product
	Pyrolysis	Thermal decomposition in the absence of oxygen	Char, gas and oil

Biochemical conversions of biomass are not cost effective owing to the fact that the biochemical techniques can solely take advantages of cellulose and hemicellulose in lignocellulosic biomass. Nevertheless, thermochemical methods are more energy

efficient and cost-effective (Pütün et al., 2006). Among the thermochemical routes, pyrolysis is the most cost effective and feasible way for the conversion of biomass into liquid fuels (Alagu et al., 2015). Pyrolysis is the thermal degradation under oxygen free atmosphere at 400 – 600 °C (Lee et al., 2014b). The principal benefit of this process potentially includes; volume of waste reduction and the retrieval of chemicals and the substitution of conventional fossil fuels (Chattopadhyay et al., 2016). During pyrolysis hemicellulose, cellulose and lignin component of biomass is converted/breakdown into a complex mixture of bio oil, gas and char. It can be carried out under a variety of conditions to capture all the components and to maximize the output of the desired product be it char, liquid or gas (Ateş et al., 2006). In general, temperature less than 400 C, in between 400 to 550 C and greater than 550C maximize the yield of char, bio oil and gas respectively.

Generally bio oil produced from pyrolysis restrict its direct application in traditional refineries and in transportation due to its high acidity, low pH, high corrosiveness, low heating value, high viscosity, instability, high oxygen content and immiscibility with petroleum fuels Iliopoulou et al. (2012); Lee et al. (2014a); (Lu et al., 2010). So it needs to be upgraded. The most feasible way to upgrade the quality of bio oil is to remove the oxygen content. Till now, two methods have been widely accepted and reported to remove oxygen content from bio oil that is hydro deoxygenation and catalytic cracking (Cheng et al., 2015; French et al., 2010). The former utilizes hydrogen to deoxygenate the oxygenated compound in the form of water, whereas the latter achieves the elimination of oxygen in the form of carbon oxides and water using shape-selective catalysts (French et al., 2010; Pütün et al., 2006). Specifically, catalytic cracking is more advantageous and attractive as it does not require hydrogen manipulation, can be used at atmospheric pressure and can be coupled with the pyrolysis process to make it cost effective and logistically appealing (Du et al., 2014; French et al., 2010; Lee et al., 2014b).

In general, catalysts are manipulated to boost up pyrolysis reaction kinetics by cracking high molecular weight compounds into lighter and more desirable hydrocarbons such as

aromatics and phenols and to enhance its calorific content (Gulab et al., 2016; Iliopoulou et al., 2014; Stefanidis et al., 2011). However, different catalyst has different cracking mechanism in different contact mode and operating conditions. In the next chapter, we will look into the catalyst employed in the field of pyrolysis, problem associated with it and possible solution to overcome this problem.

1.2 Problem statement

Pakistan is facing significant challenges in the energy sector towards meeting the demand which is increasing at a rate of 11 to 13% per year. According to approximations 60% of the total foreign exchange of the Pakistanis is consumed on importing the fossil fuels (Rehman et al., 2017).

Corn stalks were opted as biomass feedstock for this study. Annual production of corn is around 1.07 billion metric tons and is expected to increase by 16% by 2027 (OECD-FAO Outlook 2018-2027). However, in Pakistan with the annual production of 6.00 million metric tonnes (FAO report 2018) and residue to crop ratio of 2, corn is the fourth largest crop grown after wheat cotton and rice (Saeed et al., 2015). Even though corn stalks can be used as animal food, or left in the field to prevent soil erosion but its conversion into more valuable and concentrated forms of energy will be advantageous to developing countries. Pyrolysis is proven beneficial method to acquire liquid fuels from crop leftovers that are distributed broadly (Uzun et al., 2009). Furthermore, Pakistan's plastic industry is thriving at an average annual growth rate of 15%. 51% of total plastic produced is recycled and remaining 49% disposed of untreated (Chaudhry, 2010). So, to get rid of plastic and CS waste and to overcome the energy crisis (in term of fossil fuel depletion), their pyrolysis is a proficient and advantageous waste to fuel approach.

1.3 Objectives

- To optimize feedstock ratio based on high liquid yield

- To investigate the effect of catalyst to feedstock ratio in in-situ and ex-situ mode on both quantity and chemical quality of liquid oil obtained

Chapter 2 LITERATURE REVIEW

Owing to the increasing prices, depletion and environmental concerns of fossil fuels masses are shifting towards renewable energy sources. Biomass thus is a potential alternative energy source as it is abundant, cheap, CO₂ neutral and can be converted to three types of fuels that is solid, liquid and gas. Among biomass conversion to biofuel processes, Pyrolysis has received more attention recently over other technologies due to following reasons (Foster et al., 2012),

- a) It has feedstock flexibility as it can even convert feedstocks which are tough to transform into bio fuel via enzymatic processes.
- b) Biomass to biofuel conversion can be accomplished in a single reactor and in a very short time span as compared to fermentation process where detention time is mostly couple of days.
- c) Product separation can be carried out easily as the bio oil obtained from pyrolysis is concentrated as compared to ethanol generated in fermentation process.
- d) Three principal products of pyrolysis are oil (also known as bio-oil), gas and solid residue (also known as char). All of these can be employed. Gas can be burned to remove moisture from biomass and to operate reactor. Char is considered as good soil amender and oil can substitute fossil fuel (Dickerson et al., 2013).

2.1 Pyrolysis of Biomass

Biomass, particularly lignocellulosic biomass is a significant source of clean energy. It is globally available in the form of woody biomass and agricultural waste. The potential of biomass is predicted to be 1.08×10^{11} toe which is almost 10 times of the world current energy demand (Kan et al., 2016). The global availability of agricultural residues was 1394.39 million tons in 2012. Atmospheric carbon dioxide, solar energy and water are the forerunners for the synthesis of lignocellulose biomass tissues via photosynthesis. The tissues form the structure of the plant, arranged in a complex matrix in the form of

hemicellulose, cellulose and lignin. In general biomass contain 50% cellulose, 33% hemicellulose and 27% lignin and their degradation pathways are generally occur at different temperatures. Pyrolysis of hemicellulose generally take place at low temperature of 250-350 with Xylan as the principal product followed by cellulose which take place at 325-400°C with levoglucosan as the major product whereas Lignin is found very stable product and require high temperature of 350-550°C for decomposition (Kan et al., 2016).

However, Pyrolysis reactions of biomass are generally difficult to understand due to complex biomass conformations and array of reaction temperature but it can be divided into four steps namely Dehydrogenation, de polymerization, de fragmentation and rearrangement (Dickerson et al., 2013).

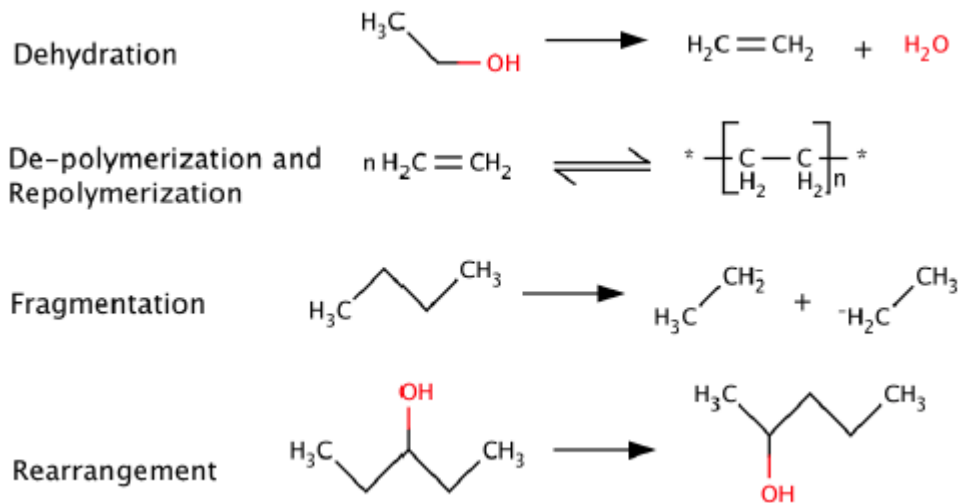


Figure 2.1 Biomass key reactions upon conversion via pyrolysis

adapted from (Dickerson et al., 2013)

As stated above pyrolysis yield all the three form of fuel solid (bio-char), liquid (bio-oil) and gas. Bio-oil as compared to fossil fuel has several environmental benefits as it is locally produced, renewable and contribute to zero SO_x , 50% less NO_x emissions and is CO_2 neutral. On the other hand char produced can be used as soil quality enhancement or can be used as activated carbon (Martínez et al., 2014). Number of factors affect the yield and properties of bio fuel such as heating rate, temperature, particle size of

biomass, biomass composition, vapor residence time, sweeping gas flow rate, type of reactor etc. Researchers have carried out pyrolysis of different biomass under different conditions to optimize the yield of bio oil.

2.1.1 Factors effecting pyrolysis of biomass

2.1.1.1 Temperature effect

Temperature of the pyrolysis is the most important governing factor which largely influence the distribution and quality of any of the pyrolysis product (Kan et al., 2016). In general, temperature of < 400°C, 400-500°C and >500 optimize the yield of char, bio oil and gas respectively. Pyrolysis of spruce wood (Demirbas, 2010) has been conducted which shows that with the increase in temperature, bio oil yield increase till 525°C afterwards further increase in temperature to 800°C decrease its yield. Contrary to it, pyrolysis of Corn Stover at high pressure of 100 Psi has also been conducted. It was found that char yield decreases with the increase in temperature. As high temperature released a major portion of volatiles from biomass particles which consequently decrease the solid residue yield. It was hypothesized that decomposition reaction of corn cob consisted of two steps; a rapid changing step, where at a temperature range of 350–400°C, most of the volatile components unchained and a slower changing step where at temperatures range of 400 to 600°C, only a part of the components begin to decompose, thus result in lower liquid yield. Moreover, at higher temperatures, rate of secondary reaction of volatiles increase, which leads to conversion of organic compound into lighter, non-condensable gases (Capunitan et al., 2012).

2.1.1.2 Sweeping gas flow rate

Flow rate of sweeping gas affect the residence time of pyrolysis vapor and subsequently affect the pyrolysis product yield and quality. Higher flow rates result in less vapor residence type within the pyrolysis setup and thus diminish the chances of secondary reaction that is re-polymerization, re-condensation (Pütün et al., 2006). It has been proved that with the increase in sweeping gas flow, gas production increase and char

production decrease as the vapors get less residence time and would not be able to get enough time for condensation (Pütün, 2010).

2.1.1.3 Heating rate

Heating rate is a fundamental parameter that describes the type of pyrolysis that is slow, intermediate and fast (Kan et al., 2016). Generally, slow heating rates with long residence time at low temperature optimize the yield of char and at high temperature optimize the yield of gas. Whereas, fast heating rate with a short residence time and moderate temperature result in high liquid yield (Duman et al., 2011). (Pütün et al., 2007) observed that fast pyrolysis yield more liquid product with more water content than slow pyrolysis and conclude that long residence time leads to secondary reactions such as dehydration, decarboxylation and condensation which ultimately reduce the water content in bio oil.

On the other hand, (Duman et al., 2011) carried out slow and fast pyrolysis of cherry seeds and found that bio-oils produced from slow pyrolysis of cheery seed can be employed as a fuel in industries and the bio-oil obtained from fast pyrolysis can be assessed as a chemical feedstock. Slow, fast and flash pyrolysis of biomass that is rapeseed has also been conducted and it was found that with the increase in heating rate from slow to flash bio oil yield has increased 45 times (Onay et al., 2003).

Table 2.1 Effect of heating rate on yield of pyrolysis products (adapted from(Yin, 2012))

Mode of pyrolysis	Temperature (°C)	Residence time	Yield %		
			Liquid	Char	Gas
Slow	400	Long	30	35	35
Intermediate	500	Moderate (10-20s)	50	25	25
Fast	500	Short (<2s)	75	12	13

2.1.1.4 Biomass pretreatment effect

Pretreatment of biomass prior to its pyrolysis has been found proficient method to enhance the yield of bio-oil. Among all the methods, chemical, physical and thermal treatment has gained more

Table 2.2 Summary showing effect of different physical parameters on pyrolysis product yields

Biomass Type	Particle size mm	Pyrolysis conditions			Yield (%wt)			Ref
		Temp °C	Heating rate °C/min	Gas flow rate ml/min	Oil	Gas	Char	
Spruce Wood	0.25-0.4	750	-	-	39.7	28.9	32.4	(Demirbas, 2010)
Spruce bark					36.3	28.5	35.2	
Corn stover	0.3-0.75	500	-	300	48.7	15.1	32.1	(Shah et al., 2012)
Corn stover	<3	400	-	-	31	15	37	(Capunitan et al., 2012)
		500			28	19	32	
		600			29	21	31	
C. inophyllum shell	0.7-4.75	350	40	n.r	38	32.5	28	(Alagu et al., 2015)
		400			41	31	27	
		450			39	33	27	
		500			36	36	26	
		550			35	37.5	25	
WS	0.18-.28	400	slow	-	45	8	46	(Ding et al., 2012)
Acid washed WS					57	4	38	
Hazelnut Bagasse	0.2-0.4	500	10	Non sweeping gas	30.7	28.5	27.8	(Demiral et al., 2006)
	0.4-0.6				33.2	29	27.9	
	0.6-0.85				32.5	29.7	27.5	
	0.85-1.8				31.9	31	27.4	
Cotton stalk	0.2-0.4	550	7	100	21	31.1	27.5	(Pütün et al., 2005)
	0.4-0.85				22	30.5	27.8	
	0.85-1.8				23.8	28.6	27.1	

	>1.8				22.5	28.5	26.6	
Cherry seed	<2	500	Slow	25	21 ^a	21	27	(Duman et al., 2011)
			Fast		44	23	18	
Rapeseed	0.4-0.85	550	Slow	100	46	27	19	(Onay et al., 2003)
	0.4-0.85		Fast		61	9	16	
	0.6-1.25		Flash		73	6	16	
Cotton seed	n.r	550	7	50	45	22	24.5	(Pütün, 2010)
				100	46	21	23	
				200	48	24	22	
				400	45	26	20	
Cotton seed cake	n.r	550	7	50	25	n.r	n.r	(Pütün et al., 2006)
				100	27			
				200	26			
				400	25.5			
Pressed bagasse	0.85-1.8	550	300	25	46.6	20.3	33	(Gerçel, 2002)
				100	46	22	32	
Soybean cake	0.425–0.6	350	10	n.r	20.4	45.8	33.7	(Şensöz et al., 2006)
		400			24.6	45.9	29.3	
		450			24.4	48.5	27.0	
		500			24.1	50.2	25.6	
		550			23.3	52.4	24.1	
		350	50		24.1	51.8	23.9	
		400			25.8	50.6	23.5	
		450			25.4	51.4	23.1	
		500			24.7	52.6	22.5	
		550			24.3	53.4	22.2	

^aWithout aqueous phase
n.r not reported

attention. The core objective of pretreatment is to alter the structure of lignocellulosic components of biomass to enhance the pyrolysis efficiency.

2.1.1.4.1 Chemical pretreatment

Alkali and alkaline earth metal in biomass, is believed to cause hindrance by increasing char formation during pyrolysis process. Moreover the presence of their salts cause corrosion of the inner reactor walls and pipeline which leads to engineering difficulties. These problems can be eradicated by reducing the ash content of biomass. The most effective method is Acid wash pretreatment of biomass, which enhance the yield and

quality of bio-oil by subsequently decreasing the mineral matter and altering the pore structure of biomass (Vamvuka et al., 2006). Ding et al., (Ding et al., 2012) found that acid washed wheat straw has less water content, high viscosity and high heating value as compared to raw wheat straw.

2.1.1.4.2 Physical pretreatment

Grinding, shredding or milling of biomass not only ease the feeding of biomass into the reactor, but also enhance the yield by distributing the temperature more uniformly within the biomass particles as smaller the particle size, the higher the heat and mass transfer rate. This uniform temperature leads to enhanced bio oil yield by subsequently reducing the char and gas formation (Demiral et al., 2006). Contrary to it, the opposite trend was observed in the pyrolysis of cotton stalk. Author has hypothesized that the larger particles have shorter residence time in the reactor due to the dragging away of the tar by the sweeping gas and resulting with the lack of time for the secondary reactions (Pütün et al., 2005). Nevertheless, particle size reduction can be expensive and considerably surge the overall cost of the process (Kan et al., 2016).

2.1.1.4.3 Thermal pretreatment

The most eminent method to pretreat the biomass thermally is Torrefaction. Torrefaction involves the heating of biomass at the temperature of 200-300°C (Van der Stelt et al., 2011). During torrefaction moisture, and light volatile extractive are completely eliminated together with a portion of hemicellulose which encompasses low thermal stability. It also leads to the partial removal of oxygen content of biomass (Ren et al., 2013). The principal supremacy of this type of thermal treatment is that it produces high calorific value bio oil than untorrefied biomass. Furthermore, it improves grind ability and combustion characteristic of biomass. (Neupane et al., 2015) found that with the increase in severity of torrefaction, aromatic yield increase.. On the other hand Bridgeman et al. (Bridgeman et al., 2010) conducted torrefaction of two biomass namely Miscanthus and willow and compared the effect of torrefaction on their grind ability behavior. It was found that with the increase in severity of torrefaction that is with the

increase in temperature, both biomass started exhibiting the grind ability behavior quite similar to that of coal whereas among both biomass torrefied miscanthus showed much more efficient and easier grind ability behavior than torrefied willow.

To compare the quality of bio oil obtained from pyrolysis of biomass, researchers have analyzed physical and chemical properties of bio oil. Table 2.3 has summarized the properties of bio oil obtained from different biomass under different condition of pyrolysis. It is obvious from the table that carbon content and HHV of bio-oil is quite low as compared to diesel. Also, oxygen content, viscosity and acid number is not meeting the requirements which lead to instability and corrosiveness and rendered its use of direct application in traditional industries or in diesel/gasoline engines. In general bio oil from biomass pyrolysis yield 35-40%wt of oxygen content in the form of acids, ketones, phenols, aldehydes, water and sugar derivative compounds (Vichaphund et al., 2015). Also from GC-MS and FTIR analysis it is concluded that bio oil is rich in acid and oxygenates which leads to low pH and low aromatic yield. So, all of the above mentioned shortcomings can be tackled by reducing the oxygen content of bio oil and reduced oxygen content of the oil can be evaluated by measuring its O/C and H/C ratios, as high H/C and low O/C ratio depict that bio oil is of higher quality.

In literature two methods have been widely reported and accepted to upgrade the bio oil (by reducing oxygen content) that is catalytic cracking and hydro-deoxygenation.

Table 2.3 summary of the properties of bio-fuel obtained from pyrolysis of different biomass

Biomass	Viscosity	Density kg/m³	C	H	N	S	O	HHV MJ/kg	H/C	O/C	Acid number mgKOH/g	MC %w/w	Ref
Diesel	2.39 mm ² /s	830	86.6	13.3		<0.2	0.01	45.5	1.84	0			(Kumar et al., 2014)
Corn Stover	-	-	78	9	1.86	0.38	10.6		1.38	0.1	23.8	12.8	(Capunitan et al., 2012)
Spruce wood	160mm ² / s	1195	69.3	8.6	0.7	-	21.4	34.3	-	-	-	-	(Demirbas, 2010)
Cherry seed shells	-	-	63.8	7.89	1.89	0.02	26.35	30.04				7.61	(Duman et al., 2011)
Cherry seeds	-	-	67.2	8.48	2.45	0.03	21.86	32.4				5.6	
Sunflower pressed bagasee	-	-	68.2	9.1	4.4	-	18.3	32.87	1.61	-	-	-	(Gerçel, 2002)
Rapeseed	-	-	73.1	11.5	4.7	-	10.7	39.4	1.89	-	-	-	(Onay et al., 2003)
Cotton stalk	-	-	56.7	6.23	1.42	-	35.7		1.32	0.48	-	-	(Pütün et al., 2005)
Tobacco residue	-	-	66.0	8.5	3.02	-	27.76	29.59	1.53	-	-	-	(Pütün et al., 2007)
Cotton seed	-	-	74.2	11.4	4.81	-	9.56	39.83	1.83	0.1	-	-	(Pütün, 2010)
Corn Stover	-	-	53	17	0.5	-	29	23	-	-	70.3	48.3	(Shah et al., 2012)

Wheat straw	13.9 at 40 (cP)	1130	34.5	8.2	0.8	-	56.5	11.7	-	-	-	46.9	(Ding et al., 2012)
Acid treated WS	23.2	1150	41.3	7.5	0.9	-	50.3	17	-	-	-	31	
Soybean cake	72.38 (cSt)	1107	67.8	7.77	10.8 4	-	13.5	33.6	1.37	-	-	-	(Şensöz et al., 2006)
Sugarcane bagasse	89.4 cst	1198	46.2	6.55	0	-	46.94	20.08	-	-	-	-	(Islam et al., 2001)
safflower seed		-	-	12.1	1.72	-	10.66	41	1.92	0.11	-	-	(Beis et al., 2002)
cashew nut shell	39cst	987	79.9	11.8	<0.2	-	8.1	40	-	-	-	3	(Das et al., 2003)
Rice Husk	128	1190	41.7	7.7	0.3	0.2	50.3	14.69	-	-	-	-	(Ji-lu, 2007)
Olive oil residue		-	-	8.62	0.62	-	21.24	32.13	1.48	0.23	-	-	(Uzun et al., 2007)
Sugarcane straw		1220	59.5	6.66	0.75	-	33.05	-	-	-	44.9	5.3	(Durange et al., 2013)
Sugarcane Natura		1220	61.2	7.13	0.69	-	30.95	-	-	-	50.6	5.5	

2.2 Upgradation of Bio-oil

2.2.1 Hydro-deoxygenation (HDO)

The hydro-deoxygenation (HDO) process has gained a lot of attention so that the unprocessed bio- oil can be converted into bio-fuel. Bio oil obtained by HDO yield 56–58% of hydrocarbons (Bridgwater, 1996). HDO is a hydrogenolysis process that eliminates oxygen from a feedstock. Carbon-oxygen bonds are cleaved with pressurized hydrogen in the presence of catalyst to generate CO₂ and H₂O and eradicate oxygen partially from the final product (Dickerson et al., 2013). The possible type of reaction involves during HDO process includes (Gollakota et al., 2016)

1. Dehydration
2. Decarboxylation
3. Hydrogenation
4. Hydrogen lysis
5. Hydrocracking

In HDO process, reactivity of catalyst depends on the strength and number of both Lewis and Brønsted acid sites on the catalyst/support system. Supports system influences both the acidity and reactivity of the catalyst (Dickerson et al., 2013). Supported Ru, Pt, and Pd are catalysts which are generally manipulated. (Elliott et al., 1991) established a two-stage incessant HDO process for the improvement of pine bio-oil. (de Miguel Mercader et al., 2011) removed the acids from bio-oil prior to HDO process, to observe the efficiency of catalytic upgrading. Ruthenium catalysts have also been used and found effective for deoxygenation (Wildschut et al., 2009; Wildschut et al., 2010). However, the criticality of the HDO methodology lies with the quantification of oxygen withdrawal.

The HDO process is found to be multifaceted and expensive due to complex equipment, catalyst addition and the high-pressure (70–200 bar) hydrogen gas necessities (Dickerson et al., 2013; Gollakota et al., 2016). Moreover, 20–30% of the carbon content present in biomass is converted in to the gas and leads to catalyst deactivation (Bulushev

et al., 2011). On the other hand, water content also reduce the catalytic activity three times of initial activity (González-Borja et al., 2011). Therefore, a new approach is required to overawe these expenses.

2.2.2 Catalytic cracking

Catalyst in pyrolysis is manipulated to speed up chemical reaction by decreasing the activation energy of the process. As, pyrolysis require high temperature so the usage of catalyst reduce the optimum temperature of the process which consequently help in saving energy (Sharuddin et al., 2016). Moreover, catalyst has also been employed extensively to upgrade pyrolysis liquid to an extent where it exhibits the same properties of conventional fuel as gasoline and diesel. Thus, Catalyst can either be manipulated offline or online. In online system, pyrolysis vapors are subjected to catalyst for cracking. In offline system bio oil is subjected to catalyst for cracking of heavy molecular hydrocarbon to lighter hydrocarbons (Abnisa et al., 2014b). The representative catalytic upgrading reactions involve (Jian Li et al., 2014)

Deoxygenation

Decarbonylation

Oligomerization

Cracking

Catalytic upgrading is an emerging technology and found to be more economical than HDO as it does not involve the addition of high pressure hydrogen gas and can be used at atmospheric pressure. Until now pyrolysis oil or pyrolysis vapor has been subjected to two types of catalyst that is heterogeneous catalyst and homogenous catalyst. As the name depicts heterogeneous catalyst involve more than one phase and homogenous involve single phase. The classical Lewis acid that is Aluminum trichloride have mostly been employed as homogenous catalyst. Whereas zeolites, basic oxides, acid solids and Nano catalyst are all examples of heterogeneous catalyst. For the upgradation of bio oil heterogeneous catalyst has been found to be more efficient as the liquid product can

easily be parted from catalyst and more cost-effective as they can be regenerated more proficiently (Sharuddin et al., 2016).

Generally, incorporation of catalyst in pyrolysis process yield gasoline range hydrocarbons that is low carbon chain compound C₅-C₁₂ with high octane number as compared to thermal pyrolysis which yield hydrocarbons of long chain carbon C₅-C₂₈ with low octane number. On the other hand it also leads to less energy demand and less temperature (Miandad et al., 2016a).

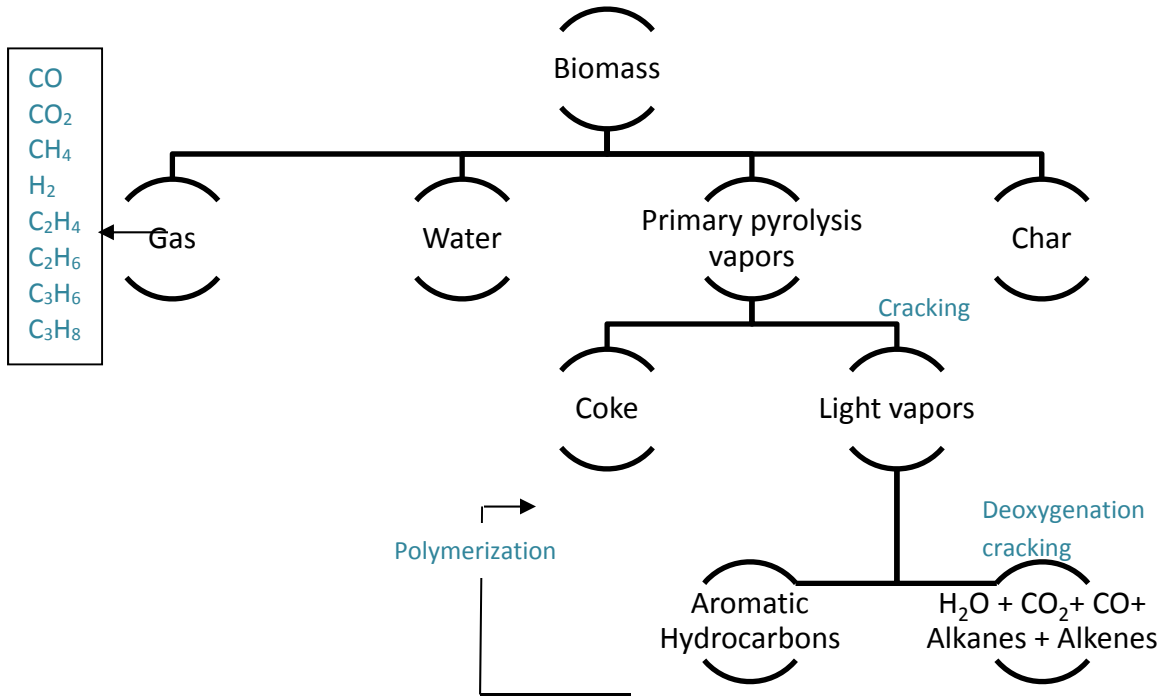


Figure 2.2 Catalytic conversion route for conversion of pyrolysis vapors with HZSM-5 catalyst
Adapted from (Zhang et al., 2009)

Researchers have not only manipulated catalyst in pyrolysis of biomass but also have seen effect of different variables such as catalyst type, temperature, loading, pore size and mode of catalyst addition on the aromatic yield of bio-oil.

2.2.2.1 Factors effect catalytic pyrolysis of biomass

2.2.2.1.1 Effect of Catalyst to feedstock ratio

Catalyst loading is an important factor to consider as it helps in making the process more economical. It largely depends on heating rate and vapor residence time. In fast pyrolysis due to short vapor residence time and hence short contact time with catalyst, large amount of catalyst is required. Contrary to it in slow pyrolysis due to more contact time of catalyst with pyrolysis vapors, small amount of catalyst can undergo the required cracking. For the catalytic slow pyrolysis of *Calophyllum inophyllum* fruit shell Catalyst to biomass (CBR) ratio was optimized for three catalysts namely zeolite, kaolin clay and alumina. Selected ratios were 1:6, 1:8, 1:10 and 1:12. For all of the above mentioned catalysts, 1:8 catalyst to feedstock ratio leads to maximum bio-oil yield of 45% approximately (Alagu et al., 2015). On the other hand, fast pyrolysis of *miscanthus X giganteus* (Du et al., 2014) at three different catalyst (ZSM-5) to biomass ratio that is 1:1, 2:1 and 5:1 has been carried out. It was found that total aromatic yield increased from 5.96% to 10.51%, total gas yield increased from 24.70% to 45.79 wt% and olefins yield increased from 7.00% to 9.93 wt% as the CBR increased from 1:1 to 5:1.

2.2.2.1.2 Effect of catalyst temperature

It is reported that at low catalyst temperature oxygen content in bio oil is removed as H₂O whereas at high catalyst temperature it is removed as CO and CO₂ (Williams et al., 2000).

In Ex situ catalytic pyrolysis of sewage sludge (Wang et al., 2017), catalytic temperature effect on aromatics, olefins and coke yield was investigated. It was demonstrated that with the increase in temperature from 400 to 800°C coke yield decrease from 13.8 to 3.11% Carbon. However olefins yield increased from 12.9 to 26.3% as the temperature increased from 400 to 700°C afterwards it decreased to 21% as temperature further increased to 800°C. Moreover, aromatics yield increased to 18% till 600°C after that it decrease. On the other hand in in situ pyrolysis of cotton seed cake (Pütün et al., 2006), by increasing pyrolysis temperature from 400 to 550°C oil yield increased afterwards it

decreased as temperature increased further to 700°C. Contrary to it, char yield was observed to be decreased drastically as temperature increased from 400 to 700°C.

2.2.2.1.3 Effect of catalyst porosity

The pore distribution of the catalyst is an eminent factor which affect product distribution considerably via diffusion limited reactions and shape selectivity (Jae et al., 2011). Based on porosity catalyst can be classified into three types, microporous (<2nm), mesoporous (2-50nm) and macro porous (>50nm). However for catalytic pyrolysis of biomass until now, microporous and mesoporous catalysts has been widely reported. It has been proposed that cracking and deoxygenation of pyrolysis vapors occur at both external and internal bronsted sites, if oxygenates are small enough to enter the micropores of catalyst. However bulky oxygenates first cracked at external acidic sites to small specie and then enter into the micro pores for further cracking into aromatics (Jian Li et al., 2014). Catalytic pyrolysis of *Laminaria japonica* (Lee et al., 2014b) using three different microporous catalyst namely HY, HBETA and HZSM-5 with pore size of 0.74nm, 0.66nm and 0.55nm respectively has been reported. It was concluded that manipulation of HZSM-5, due to strongest bronsted acidity and small pore size, yield more gas and aromatics. As smaller the pore size more will be the cracking of intermediate oxygenates into light hydrocarbons in the range of C₁-C₄. Furthermore largest acidic compound (which can cause corrosion of transfer lines) removal has also been observed by HZSM-5 again due to its high acidity. On the other hand, (Foster et al., 2012) found that with the increase in mesoporous volume coke production increase. Contrary to (Jian Li et al., 2014) concluded that increase in meso porosity (from 0.058 to 0.127 mL/g) via desilication decrease the coke yield by improving the diffusion property of catalyst in the pyrolysis of biomass which produce bulky oxygenates.

2.2.2.1.4 Effect of SAR of catalyst on yield

Silica to alumina ratio govern the acidity of catalyst. Lower the SAR, higher is the acidic site (Lewis and Bronsted) present in the catalyst. Among acidic sites, bronsted acidic

site has always been considered and found active in conversion of pyrolysis vapor to high value aromatics (Carlson et al., 2010; Zhu et al., 2010). (Foster et al., 2012) synthesized ZSM-5 with four different SAR 23, 30, 50, and 80 having micro pores volume of around 0.12 cm³/g and mesoporous volume of 0.029, 0.056, 0.059 and 0.077 cm³/g respectively. They observed the potential of converting pyrolysis vapors into aromatics and found maximum aromatic and CO yield and minimum coke production for 30 SAR. So, 30 SAR has proven optimum due to presence of large number of bronsted acidic site which at the same time maintain the distance between them so that coke forming reaction may restricted. Similarly Lee et al., (Lee et al., 2014b) tested HZSM5 with SAR of 23 and 80 and found that SAR of 23 yield more aromatics, less undesirable hydrocarbons and less acidic compounds due to its high bronsted acidic sites and characteristic pore size. Similar results has been obtained by (Stefanidis et al., 2011) that with the increase in acidity of ZSM-5 and Alumina catalyst, aromatic yield increase and oxygen content decreases.

2.2.2.1.5 Effect of mode of catalyst addition

Based on arrangement of catalyst and feedstock, catalyst mode of loading is classified into two types (Hu et al., 2017; Wang et al., 2017).

- (a) In situ where catalyst is placed in same reactor as of feedstock by physically mixed with feedstock
- (b) Ex situ where catalyst is located downstream of pyrolysis reactor in a separate reactor, commonly called as catalytic reactor

Researchers have carried out both In-situ and Ex-situ catalytic pyrolysis of biomass and found that in situ yield more aromatics and ex situ yield more olefins. The preferable configuration found from extensive studies of both the configuration is ex situ as (Hu et al., 2017; Wang et al., 2017)

- (a) Temperature of catalyst can be controlled independently

- (b) Catalyst deactivation due to alkali alkaline earth metals (present in biomass) can be eradicated.
- (c) Separation of char from catalyst is not required, thus char can be obtained as useful byproduct

From all of the above discussion and table 2.4 we came to a conclusion that zeolites are most effective catalyst in improving the quality of bio oil by converting oxygenated compounds to aromatics hydrocarbons (gasoline range compounds) and also assist in lessen the molecular weight of bio oil (French et al., 2010; Stefanidis et al., 2011). However among zeolites HZSM-5 has shown high yield of aromatics due to its shape selectivity and high surface area. HZSM-5 has three dimensional micro pore structure with a pore size of 0.51-0.56 nm similar to kinematic diameter of BTEX which subsequently leads to higher yield of these hydrocarbons (Hu et al., 2017; Vichaphund et al., 2015). Furthermore, it also leads to less coke formation as compared to other catalysts due to its high Bronsted acidity and appropriate pore size.

Although the induction of HZSM-5 in pyrolysis of biomass yields high aromatic compounds, but due to formation of coke on the catalyst surface, it deactivates quickly and do not perform the desired cracking. Coke is mainly formed due to dehydration of oxygenated compounds having high oxygen content. French et al., (French et al., 2010) demonstrated that during pyrolysis of aspen wood ZSM5 indicated good deoxygenation of pyrolysis vapor first four minutes. After that zsm-5 had been partly deactivated. The reason concluded by author was low hydrogen effective index of aspen. In order to eradicate this problem, researchers have found that mixing of biomass with the feedstock having high hydrogen to carbon effective ratio, is the most proficient way. Thus co pyrolysis of biomass with plastic has been conducted widely.

Table 2.4 Summary of the catalytic pyrolysis of biomass

Biomass	Catalyst	Heating	In/E x	CBR	P temp	C Temp	Oil	Gas	Char	Coke	Findings	Ref
prairie cordgrass	Non-catalytic	Slow	Ex situ	0.01	500	500	29	44	26	n.r	With catalyst addition no significant difference in yield of oil and gas was observed HZSM-5 yield more hydrocarbons and less phenols than Ni/HZSM-5	(Cheng et al., 2015)
	HZSM-5						24	44	32			
	Ni-HZSM-5						25	44	33			
lignocellulosic biomass	Non-catalytic	Flash	In situ	0.46	500	500	58.9	17.7	23.4	n.r	Non catalytic pyrolysis yield more bio-oil and less gas as compared to catalytic pyrolysis. Co-ZSM5 significantly increase the aromatic and decrease the oxygen content of the bio-oil as compared to ZSM-5	(Iliopoulou et al., 2014)
	ZSM-5						46.5	27.0	26.5			
	Co-ZSM-5						42.6	31.1	26.3			
Calophyllum inophyllum fruit shell	Non-catalytic	Slow	In situ	0.125	400	400	41	32	26	n.r	Zeolite catalyst was found most effective in improving the calorific value (by reducing the oxygen content of pyrolysis vapors) and pH (by reducing the water content)of the bio oil as compared to non-catalytic and other catalyst employed (kaolin and alumina).	(Alagu et al., 2015)
	ZSM-5						44	36	20			
	kaolin						45	34	21			
	Al ₂ O ₃						45	35	20			
Wastewater sludge	HZSM-5	Fast	Ex situ	20	500	600	19.1 24.4	10	33	10	With the increase in pyrolysis temperature from 400 to 800C, there was no significant effect on coke yield was observed. However, with the increase in catalyst temperature from 400 to 800C coke yield decrease significantly by 23%. Char obtained can be used for soil amendment after removal of heavy metals	(Wang et al., 2017)

Cotton seed cake	Zeolite	Slow	In situ	0	550	550	26	n.r	n.r	n.r	With the increase in catalyst loading, oil yield increase significantly With the addition of 20% zeolite calorific value increase to 33.34 MJ/kg as compared to non-catalytic bio oil which has calorific value of 30.96MJ/kg	(Pütün et al., 2006)
				0.01			26.3	22	27			
				0.05			27.7	21	26.5			
				0.1			29.5	21	25.5			
				0.2			30.8	20	25.2			
Laminaria japonica	Non-catalytic	Slow	Ex situ	0.1	500	500	32.9	24.7	42.4	n.r	Catalytic pyrolysis yield less oil as compared to non-catalytic owing to higher cracking ability of all the catalysts. Among all catalysts employed HZSM-5(23) enhanced the yield of High Value aromatics (i.e furans, cyclopentane) and decrease the acidity of bio-oil. Furthermore, Oxygenates also decrease with HZSM-5 (23) due to its strong bronsted acidity and small pore size.	(Lee et al., 2014b)
	HZSM-5 (23)						24.5	33.1	42.4			
	HZSM-5 (80)						29.4	27.8	42.8			
	HBETA						26.3	31.1	42.6			
	HY						26.8	30.8	42.4			
Citrus unshiu peel	Non catalytic	n.r	Ex situ	1	500	600	36	28	~35	0	Increase in temperature leads to increase in aromatic yield from 3.25 to 5.96%wt. Furthermore, with the increase in temperature MAH increased due to promotion of decomposition reaction at higher temperature which consequently produce smaller compound which can easily penetrate into the ZSM-5 pores and also leads to high gas yield	(Kim et al., 2015)
	ALMCM-41						22	36		4		
	HY						12	42		9		
	HBETA						16	41		8		
	HZSM-5 (50)						18	45		2		
	HZSM-5 (23)						18	44		3		
miscanthus giganteus	ZSM-5	Fast	In situ Ex bed	1	400	400	42	15	43	n.r	Increase in temperature leads to increase in aromatic yield from 3.25 to 5.96%wt. Furthermore, with the increase in temperature MAH increased due to promotion of decomposition reaction at higher temperature which consequently produce smaller compound which can easily penetrate into the ZSM-5 pores and also leads to high gas yield	(Du et al., 2014)
					500	500	40	14	36			
					600	600	33	20	35			
glucose	ZSM-5(23)	Fast	Insitu	19	600	600	29	26	n.r	39		

	ZSM-5(30)						40	24		33	As the SAR increase, acidity increase, which leads to high aromatic yield and low coke yield but further increase in SAR decrease the aromatic yield and increase the coke yield Catalyst with high mesopore volume produce more coke and heavy MAH as compared to microporous catalyst.	(Foster et al., 2012)
	ZSM-5(50)					32	18		37			
	ZSM-5(80)					25	21		40			
Pine wood chips	Non-catalytic	Slow	Insitu Ex bed	0.4	450	450	32.7	52	15.3	0	Among all the catalyst used, HZSM5 is found proficient in increasing the yield of oil and gas and decreasing the yield of coke. Furthermore, acids which cause corrosion of pipelines, also get reduced significantly by HZSM-5	(Aho et al., 2008)
	H Beta						29	49.5	10.4	11.2		
	HY						25.7	51.1	6.5	16.7		
	HZSM-5						33.7	52.1	9.0	5.2		
	HMOR						32	48.1	12.7	7.2		
Corncob	Non-catalytic	Fast		5	550		33.9	14	23.2	2	Although the oil yield decrease in the presence of catalyst but Aromatic hydrocarbons increased remarkably in the presence of catalyst. Moreover manipulation of catalyst also leads to decrease in acids and oxygen content of bio oil.	(Williams et al., 2000)
	HZSM-5						13.7	26	21	8.4		
Rice Husk	Non-catalytic	n.r	Insitu Ex bed	1	550	400	28.5	25.4	26.8	0		
	ZSM-5						7.2	22	30.5	12		
Alcell Liginin (AL)	Nano NiO	Fast	Insitu	0%	550	550	49.9	7.6	42.5	n.r	With the increase in catalyst ratio, bio oil yield increased first and then decreased. So, the optimum catalyst percentage found was 10%. In comparison to non-catalytic pyrolysis, catalytic pyrolysis yield more aromatics and less oxygenates and has higher HHV with optimum CBR ratio	(Chen et al., 2015)
				5%			52.9	8.3	38.7			
				10%			53.1	11.2	35.7			
				15% of AL			52.2	12.8	35.0			

2.3 Co Pyrolysis of Biomass

Co pyrolysis is a technique which comprise two or more than two dissimilar materials as a feedstock. The effectiveness of this technique is governed by synergistic effect. It generally portrays the interaction of two or more dissimilar materials which when combined together produced a full effect that is larger than the addition of the effects or contributions from the solo co-feeding material which leads to either in upgradation of the quality and quantity of the subsequent products or result in deteriorating of any attribute of the output material (Abnisa et al., 2014b). Usually, it involve the addition of biomass (hydrogen deficient and oxygen rich material) with plastic or waste tires (hydrogen rich material).

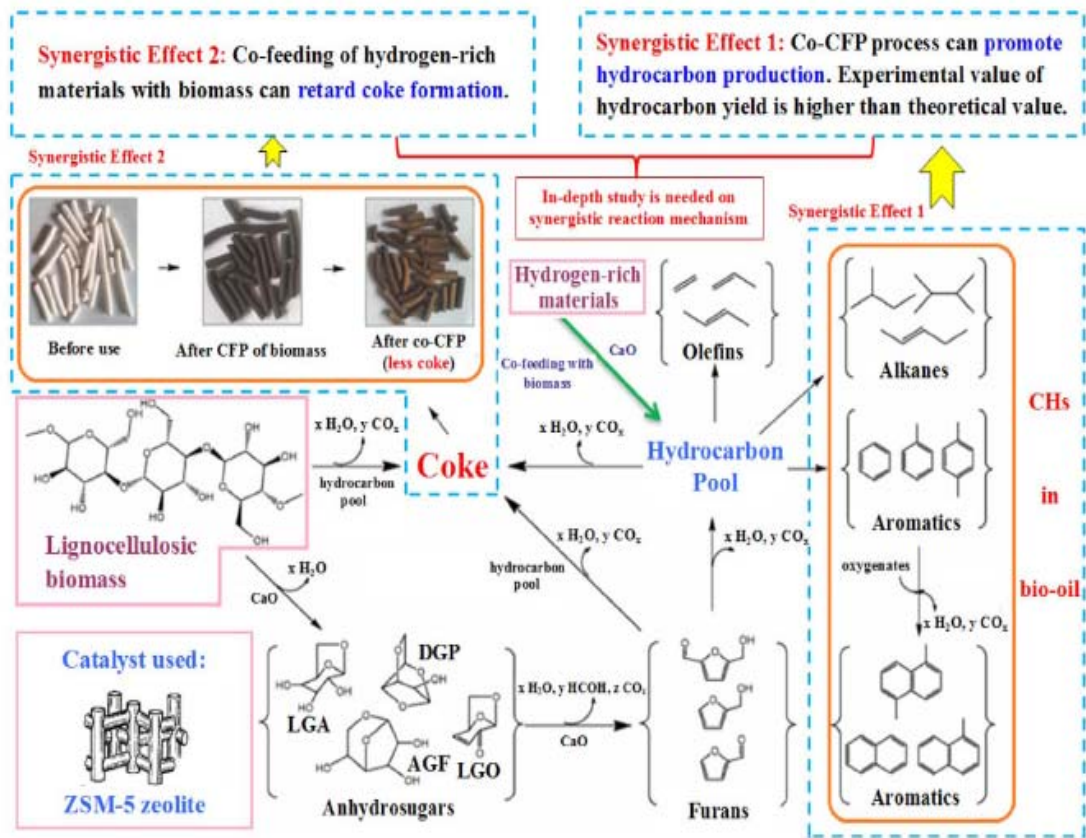


Figure 2.3 Schematic diagram of synergistic effects during co-pyrolysis of biomass and Plastic adapted from (RP 14 (hera wala))






Separate pyrolysis of biomass and plastic not only need more energy, more cost and more time but also the blending of bio oil obtained from pyrolysis of plastic/waste tire and biomass alone cannot be mixed homogenously due to polar nature of plastic/waste tire bio-oil. Thus co pyrolysis found to be more proficient and reliable technique to get homogenous bio oil (Hassan et al., 2016). Additionally, it also contribute to waste management as more waste is used as feedstock which in turn not only reduce the volume of waste sent to landfill but also save the cost for waste treatment and protect the environment.

Waste tires has been investigated extensively as a co feedstock with biomass. However the major attention now a days have been shifted to pyrolysis of plastics as Plastics are highly desired matter utilized in a broad range of applications owing to its flimsy nature, high resistivity to chemical reactions and lower bio degradability (Sharuddin et al., 2016). Furthermore, recycling of all plastic waste is not possible and incineration of plastic waste produce dioxins which deteriorate environmental quality. Besides, dumping of plastic waste in landfill not only pose a great pressure on landfill area but also results in a major resource loss (Miandad et al., 2016a).

Thus among various technique to process plastic waste, pyrolysis is gaining immense attention to use plastic as a co feedstock in catalytic conversion of biomass to bio-oil (Brebun et al., 2010). Also, when pyrolysis of plastic and biomass carry out simultaneously, the bio oil stability always anticipated to be significantly enhanced as compared to that which is formed by single biomass pyrolysis, as plastic donate ample amount of hydrogen to the biomass during pyrolysis (Önal et al., 2014). The main advantage of using plastic is to enhance the hydrogen content of feedstock which in turn reduce the coke deposition on catalyst as coke deposition is a major cause of catalyst deactivation. Current world-wide production of plastics is around 300 million tons/year (Ratnasari et al., 2017) and until now all the plastics for pyrolysis has been investigated.

It is clear from table 2.5 that polystyrene, high and low density polyethylene and polypropylene has largest potential of converting into bio-oil upon pyrolysis.

Table 2.5 Summary of suitability of Plastic for pyrolysis process; adapted from (Miandad et al., 2016a)

Symbol	Polymer Name	Recyclable curbside	Suitability for pyrolysis	Comments
	Polyethylene tetra ethane	Yes	Not appropriate	It encompasses heteroatoms
	Polyethylene	Yes	Very Good	Require high temperature During thermal pyrolysis it is converted into wax During catalytic pyrolysis it leads to high aromatic yield
	Polyvinyl chloride	No	Not acceptable	Release chlorine gas, which is hazardous
	Polypropylene	Yes	Good	Contain ample amount of hydrogen, thus leads to high aromatic yield and less coke formation on catalyst After PE it is difficult to degrade PP thermally
	Polystyrene	No	Excellent	Require low temperature, produce more quantity and low viscosity of bio oil as compared to PP and PE

2.3.1 Catalytic co pyrolysis of plastic and Biomass

As stated earlier, synergistic effect between biomass and plastic is the key of co pyrolysis process. Thus, apart from all of the above stated factors see section 2.2.2.1 synergistic effect during co- pyrolysis process is principally affected by composition of individual feedstock used and blending ratio of feedstock.

2.3.1.1 Composition of plastic

Fundamentally, different type of plastic has different composition which is normally reported in term of their proximate and ultimate analysis. Proximate analysis of plastic is the major factor which gives us the idea of potential of conversion of plastic into bio-oil. Proximate analysis is a technique which involve partitioning of a compound present in feedstock into four categories based on chemical properties of the compound. The four categories are named as Moisture content, Fixed carbon, Volatile matter and ash. Generally, high volatile matter increase the formation of bio-oil where as high fixed carbon and ash content leads to formation of char (Sharuddin et al., 2016). On the other hand ultimate analysis of feedstock gives the idea of hydrogen to carbon effective ratio, which is an important factor, as discussed earlier to decrease the formation of coke on catalyst. The term hydrogen to carbon effective ratio is defined on the assumption that all the heteroatoms present in feedstock completely converted into water, ammonia and hydrogen sulfide. It is usually calculated as

$$\frac{H}{C_{eff}} = \frac{H - 2O - 3N - 2S}{C}$$

Where H, N, O, C and S are the mole number of hydrogen, nitrogen, oxygen, carbon and sulfur respectively.

Table 2.6 Literature of proximate and ultimate analysis of different plastics

Plastic	VM	FC	Ash	C	H	N	S	O*	H/C _{eff} ^a	Ref
HDPE	99.8	0.01	0.18	84.7	11.6	0.02	0.66	2.93	1.59	(Ahmad et al., 2013)
	99.4	0	0.34	81.4	12.1	0.34	0.79	5.36	1.67	(Chin et al., 2014)
LDPE	99.9	0	0.1	85.9	14	-	-	-	-	(Gunasee et al., 2017)
	99	0	0	85	15	0.1	0.1	0.01	2.11	(Dewangan et al., 2016)
PP	99.9	0.09	0.01	83.1	11.8	0.14	0.16		-	(Ahmad et al., 2015)
	80	20	0	85.8	14.2	-	-	-	-	(Zhang et al., 2014)

PS	99.1	0.39	0.04	92.1	7.72	0	0.26	0	1.00	(Wu et al., 2014)
	99.5	0.5	0	92.2	7.8	-	-	-	-	(Zhang et al., 2014)

*calculated based on difference

^aCalculated based on formula $\frac{H}{C_{eff}} = \frac{H-2O}{C}$

Generally, biomass has H/C_{eff} ratio in the range of 0 to 0.4 and according to literature feedstock having H/C_{eff} ratio of <1 is considered ineffective to convert pyrolysis vapors into hydrocarbons and leads to rapid catalyst deactivation (French et al., 2010). Zhang and his coworkers carried out catalytic pyrolysis of ten different biomass of different H/C_{eff} ratio using ZSM-5 in a Fixed bed reactor and concluded that yield of aromatics and olefins increase with the increase in H/C_{eff} ratio of biomass (Zhang et al., 2011). So it becomes crucial to mix the hydrogen deficient feedstock with hydrogen rich feedstock. Thus plastics (having H/C_{eff} of 1 to 2.1) addition in biomass is considered effective in enhancing the H/C_{eff} of resultant feedstock.

2.3.1.2 Effect of blending ratio

In order to evaluate the effect of hydrogen donor, plastic and biomass are mixed in various proportions. Researchers have carried out non catalytic co pyrolysis of biomass and plastic (Ojha et al., 2015a) with different blend ratio more extensively as compared to catalytic. In Non-catalytic co pyrolysis of pine and waste plastic (Paradela et al., 2009a) it was found that with the increase in pine content in mixture liquid yield decrease however gas and char yield increase. On the other hand hydrocarbon yield also decreased with the increase in pine content. Same conclusions were derived by Paradela and his coworkers (Paradela et al., 2009b).

Ex situ catalytic Co pyrolysis of cellulose and LDPE with mixing ratios of 4:1, 2:1 and 1:1 using ZSM-5 has been carried out (Xiangyu Li et al., 2014). Maximum petrochemical yield that is sum of aromatics and olefins were achieved at 2:1. However coke yield decrease with the increase in LDPE content in blend ratio. Co pyrolysis of Corn stalk and HDPE (Zhang et al., 2015a) led to increase in aromatic yield with the

increase in HDPE content in mixture. Highest hydrocarbon yield was obtained at biomass to HDPE ratio of 1:4. Furthermore, coke yield was found to be decreased with the increase in hydrogen to carbon effective ratio. Significant synergistic effects have been perceived between paper biomass and plastic mixture during pyrolysis reaction, bring about inclination of liquid products of the blend encompasses more plastic. Contrary to it, gas and char production followed the reverse trend. Highest yield of aromatics and olefins and thus petrochemicals has been obtained at biomass to plastic ratio of 1:5 (Chattopadhyay et al., 2016). Similar trend was observed by (Zhang et al., 2014) in the catalytic co pyrolysis of pine saw dust and PE in a fluidized bed reactor. Coke yield has also found to be decreased with the increase in PE proportion in blend.

Chapter 3 MATERIAL AND METHODS

3.1 Materials

3.1.1 Feedstock preparation and characterization

Corn stalks were obtained from a farm field of Haripur, located in province of Punjab, Pakistan. Afterwards stalks were sundried for 24 hrs to remove peripheral moisture content followed by grinding in high speed rotary cutting mill/mechanical crushing and sieving through 40 mesh. Prior to experiment, biomass was dried in oven at 105C overnight to prevent moisture condensed onto pyrolysis products. Polystyrene beads of 1mm purchased from Madina Styrofoam Islamabad were used as received without any processing.

Proximate analysis, ultimate analysis, HHV and bulk density of feedstock were analyzed in accordance with ASTM D3172-07, ASTM D7291-96, ASTM D5865 (6200 parr isoperibol bomb calorimeter) and ASTM D1895B standards respectively. However compositional analysis of biomass sample including Cellulose, hemicellulose and lignin content were approximated via ASTM D1103, ASTM D1104 and ASTM D1106 respectively.

To determine degradation behavior of feedstock with respect to temperature thermogravimetric analysis (TGA) had also been performed using Mettler Toledo TG analyzer. 4.2 mg and 5.3 mg of biomass and plastic was taken individually in aluminum oxide crucible and heated from room temperature to 600°C with the heating ramp of 20 °C/min under inert atmosphere.

3.1.2 Catalyst characterization

Commercially available pellets of ZSM-5 in protonic form with silica to alumina ratio of 38 were purchased from Gongyi City Meiqi industry and trade co., ltd, which were then crushed and sieved to 50-70 mesh size. Prior to each experiment catalyst was calcined in muffle furnace at 500C for 5 hrs to activate it.

Textural properties of catalyst HZSM-5 were found by N₂ adsorption-desorption isotherm obtained at 77K using micromeritics Gemini VII surface area and porosity analyzer. Prior to analysis, catalyst was degassed under vacuum at 300C for 8 hrs. The specific surface area was then calculated from linear portion of BET plot (P/P₀=0-0.35). Total pore volume was determined by volume of gas adsorbed at relative pressure (P/P₀) of 0.99. Whereas, Micro and meso pore volume was obtained by t-plot and difference (V_t- V_{micro}) method respectively.

Powder XRD pattern to confirm the crystalline structure of catalyst was generated by X-ray diffractometer (θ - θ STOE Germany) using Cu-K α (λ = 0.15406 nm) as radiation source at 40 KV and 40mA. The catalyst was scanned at 2θ from 5-55° with the scanning speed and step size of 1 sec/step and 0.04° respectively.

3.2 Experimental setup

A Lab scale fixed bed reactors; pyrolysis and catalytic made up of 316 stainless steel was commissioned for in situ and ex situ catalytic co pyrolysis. Fig 3.1 represent the schematic diagram of the system. Both the reactors were heated externally by electric ceramic band heater and thermally insulated by mica sheet followed by ceramic wool and thermal cloth. The temperature of both reactors were monitored by K type thermocouple which is inserted in the middle of the reactor and controlled by PID to maintain the temperature by limiting it to the preset value.

Table 3.1 Setup Components and features

Setup components	Features
Height of pyrolysis reactor	50.8cm
Internal Dia of pyrolysis reactor	10.4cm
External Dia of pyrolysis reactor	11.8cm
Working Capacity of pyrolysis reactor	200g
Height of catalytic reactor	36cm
Internal Dia of catalytic reactor	4.2cm
External Dia of catalytic reactor	4.8cm
Maximum bed height capacity	11cm
Condenser length	2.5ft
Condenser diameter	6mm

Prior to experiment all the setup components were purged with inert nitrogen gas at flowrate of 300ml/min which was controlled by rotameter and continued for 45 minutes to remove all the oxygen present in the system. However during experiment, Nitrogen gas with the flow rate of 50ml/min was used as sweeping gas to maintain anoxic environment inside the reactors and to sweep the pyrolysis vapors from reactor to condensation system. Condensation system was made up of copper tube and kept at -6C via ice and NaCl.

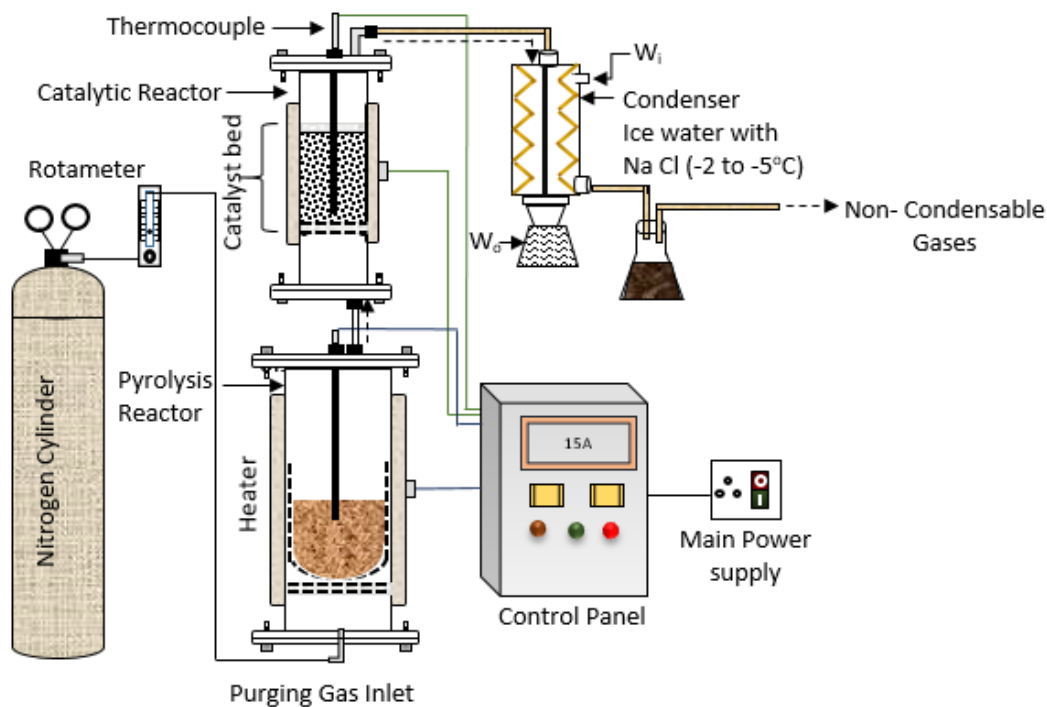


Figure 3.1 Schematic diagram of pyrolysis setup

For in situ experiments, feedstock and catalyst were mixed manually to obtain homogenous mixture and then inserted/transferred into the pyrolysis reactor while catalytic reactor was kept empty and held at 500°C to prevent the tar formation. The amount of feedstock taken in all experiments was 100grams, placed in stainless steel mesh crucible and held at its place by wire netting placed below it. With the heating rate

of 30°C/min, the reactor was heated from room temperature to pyrolysis temperature and kept there for either a minimum of 30mins or till no more notable release of gas was witnessed. Liquid product obtained after condensation of pyrolysis volatiles were collected and quantitatively measured in pre weighted flask. After the experiment, heaters were switched off and reactors were allowed to cool down to room temperature (in order to avoid the oxidation of char) and then dissembled to obtain the weight of char. Weight of char was measured by deducting the weight of catalyst used from total amount of residual obtained whereas weight of gaseous fraction was calculated by difference.

For ex situ experiments catalyst was placed in catalytic reactor on pair of air distribution plate which is #100 stainless steel wire netting, with ceramic wool in between and also covered by ceramic wool to prevent the carryover of the catalyst with sweeping gas. The pyrolysis vapors evolved in this case passed through the catalytic bed located in the catalytic reactor which had previously been heated and held to 500°C. In case of ex situ coke is measured as weight of catalyst before the experiment subtracting weight of catalyst after the experiment and gas yield is measured by following eq,

$$\text{Yield of gas} = \text{Mass of feedstock taken} - \text{Mass of oil} - \text{Mass of Char} \\ - \text{Mass of coke}$$

All the experiments were carried out in duplicate and average values were taken. Furthermore, reactors were washed by acetone at the end of experiment. The liquid product obtained consist of two phase; dark brown, viscous liquid hereby termed as organic phase and opaque to light yellowish liquid known as aqueous phase. To separate two phases, bio-oil was centrifuged at 1500 RPM for 30 Minutes in refrigerator centrifuge (Centurion Scientific K3 Series). Afterwards, organic and aqueous phase were separated via decantation. Organic phase was filtered through anhydrous sodium sulfate bed to remove traces of water, if present. This organic phase was then subjected to analysis.

3.2.1 Experimental Scheme

Experimental runs were conducted in three phases.

Phase 1 Corn stalk and polystyrene were pyrolyzed in five different blend ratios; 1:0, 1:3, 1:1, 3:1 and 0:1. Ratio which yield maximum bio oil was selected for the next two phases.

Phase 2 In situ catalytic upgrading of pyrolysis vapors was conducted with catalyst to feed stock ratios of 0.1, 0.25, 0.5, 0.75 and 1

Phase 3 Ex situ catalytic upgrading of pyrolysis vapors was conducted with catalyst to feed stock ratios of 0.1, 0.25, 0.5, 0.75 and 1

Afterwards, all the bio oil samples obtained from In-situ and Ex-situ catalytic co pyrolysis were analyzed by GC-MS and compared with non-catalytic one. Bio-oil with highest aromatic yield was then subjected to further analysis.

3.3 Liquid Oil Characterization

Gas chromatograph-mass spectroscopy (QP2010 Ultra) equipped with DB-5 MS chromatographic column (Length 30m, thickness 0.25 μ m and diameter 0.25mm) was employed to analyze the composition of liquid product. 0.2 μ l of sample was injected into injection port maintained at 285 $^{\circ}$ C in a split ratio of 80:1. With the flow rate of 1ml/min helium gas was used as carrier gas in order to operate the column in constant flow mode. The column temperature was initially set at 30 $^{\circ}$ C for 1 min and then with the heating rate of 8 $^{\circ}$ C/min, it is programmed to increase to 290 $^{\circ}$ C and held there for 2 min. The detector interface temperature was kept at 295 $^{\circ}$ C. To dilute the liquid oil to a concentration appropriate for analysis Tri chloro methane was used as solvent. Chemical compounds were identified by comparing spectra obtained with standard spectra in NIST data library 11 and a semi-quantitative technique was applied to analyze the relative proportion of each chemical component present in the liquid products.

Physical properties including Specific gravity, Density, Flash point and Pour point, of the optimized liquid product was determined according to ASTM D4052-96, ASTM

D4052, ASTM D7236 and ASTM D97, respectively. In addition, Kinematic viscosity and HHV of liquid oil was acquired using red wood viscometer and 6200 parr isoperibol bomb calorimeter according to ASTM D244 and ASTM D240 methods respectively.

3.4 Synergistic effect calculations

During non-catalytic co-pyrolysis synergistic interaction is the main governing factor and is calculated by comparing the experimental yields with calculated theoretical yield. Theoretical yield was calculated by below mentioned formula with an assumption that no interaction among pyrolysis vapors were observed,

$$Y_t = xY_{ep} + (1 - x)Y_{eb}$$

Where Y_t is theoretical yield, x is blending ratio of plastic, Y_{ep} and Y_{eb} is the yield of the pyrolysis product with plastic alone and biomass alone respectively.

And the synergistic effect was calculated by the following equation

$$\Delta S = Y_e - Y_t$$

(Martínez et al., 2014) and (Çepelioğullar et al., 2014) emphasized that positive difference between experimental and theoretical yield elucidate significant interaction between aforementioned feedstock to increase the certain pyrolysis product yield. Whereas, negative difference depicts no synergistic effect. Furthermore, the extent of deviation implies the extent of synergistic effect.

Chapter 4 RESULTS AND DISCUSSIONS

4.1 Feedstock Analysis

Table 4.1 presents the characterization results of biomass and plastic. Proximate analysis of corn stalk and polystyrene depicts that it comprehend high volatile matter and less ash and moisture content respectively. (Dewangan et al., 2016) observed that high volatile matter renders high volatility and reactivity which is advantageous for enhancing liquid oil yield. However, high ash and fixed carbon content decrease oil production and promote char and non-condensable gas yield. Whereas, less moisture content increases conversion efficiency and reduces the water content in oil which subsequently enhances its calorific value (Shadangi et al., 2014).

Ultimate analysis of biomass corn stalk reveals that it contains relatively low carbon and hydrogen content which gives it hydrogen to carbon effective (H/C_{eff}) ratio of 0.14. As various researchers have found that H/C_{eff} of less than 1 leads to enhanced coke formation during zeolites upgrading that ultimately causes rapid catalyst deactivation (Xiangyu Li et al., 2014). Therefore, blending of corn stalk with hydrogen rich feedstock to boost up catalyst performance becomes crucial. It can be perceived from table 1 that PS H/C_{eff} ratio is greater than that of CS hence hydrogen donation from PS to CS during co-pyrolysis reaction is anticipated. Additionally, oxygen content of CS is much greater than PS which is the key reason for the low calorific value of CS (Abnisa et al., 2014a).

Compositional analysis of biomass disseminate that hemicellulose, cellulose and lignin compose the structure part of biomass. It is inferred that each component's pyrolysis exhibits distinctive thermochemical properties and reactions pathway and enhance the yield of different pyrolysis products (Kabir et al., 2017). Hollocellulose content favors liquid oil production and lignin contributes to char formation (Ding et al., 2012; Shadangi et al., 2015). Furthermore, high lignin content increases the viscosity but reduces the water content of obtained liquid oil (Kan et al., 2016). The % weight of composition of biomass as depicted in table are close to those reported in literature

(Capunitan et al., 2012; Zhang et al., 2015b). The HHV of corn stalk and polystyrene representing their respective energy content and in line with literature (Guo et al., 2015; Williams et al., 1997) .

Table 4.1 Feedstock analysis results

	Corn Stalk	Polystyrene
Proximate analysis^a		
Moisture content (MC)	6.45	0.2
Volatile matter (VM)	73.8	98.8
Ash	5.8	0.3
Fixed Carbon (FC)	13.92	0
Ultimate analysis^b		
C	47.49	90.4
H	6.12	8.57
N	0.8	0.4
S	0.1	0.03
O*	45.49	0.6
Compositional analysis		
Hemicellulose	33.24	
Cellulose	37.26	
Lignin	12.71	
HHV (MJ/kg)	15.7	42.3
H/C _{eff}	0.11	1.13
Empirical Formula	CH _{1.54} N _{0.01} O _{0.7} S _{0.001}	CH _{1.14} N _{0.004} O _{0.005} S _{0.0001}
Bulk Density (g/cm ³)	0.169	0.61

^adry basis

^bdry and ash free basis

^cbased on difference

TGA curves of feedstock corn stalk and polystyrene are visualized in fig . As mentioned earlier, corn stalk is lignocellulosic biomass composed of hemicellulose, cellulose and lignin so its decomposition exhibited three stage mass loss pattern whereas PS portrayed one-stage decomposition pattern, as it is long chain polymer. It is observed that decomposition of CS started earlier as compared to PS due to its low thermal stability. The first stage mass loss of CS (4.1%), started from room temperature and continued till 200°C, is associated with elimination of moisture adsorbed on sample. The intermediate stage decomposition as seen by sharp bend occurred within a temperature range of 220-380°C contributed to the maximum weight loss of 50% which is linked with loss of

hollocellulose content of biomass. This inferred that the pyrolysis key reactions including dehydration, de-polymerization, decarboxylation and cracking take place within this temperature range (Uzun et al., 2009). Afterwards the final stage decomposition occurred between 380°C to 600°C with the maximum weight loss of 14% is attributed to loss of lignin. It is noteworthy that final residue (31.9%) left is higher than those mentioned in previously reported studies (Lv et al., 2010; Uzun et al., 2009) which may be attributed to difference in mineral matter content and macromolecular components of biomass.

Whereas, in case of polystyrene negligible mass loss till 280°C was visualized. This affirm that no moisture content was adsorbed on PS beads and it remained thermally stable up to 280°C. The major mass loss of 99% was noticed in a narrow temperature range of 280°C to 410°C which is considered as active pyrolytic zone and attributed to its de-volatilization. It is worthwhile to note that PS decomposed completely without leaving any residue.

It is reported that elected pyrolysis temperature must be greater than degradation temperature at which maximum mass loss for each feedstock is observed (Elsayed et al., 2016). Thus as a consequence of above mentioned TGA results, 500°C is concluded appropriate temperature for pyrolysis and co-pyrolysis of CS and PS as maximum mass loss was observed till this temperature.

4.2 Catalyst characterization

Surface and textural properties of catalyst HZSM-5 are given in table. Average pore diameter reveals that it is mesoporous as meso pore diameter is in range of 2-5nm (Artetxe et al., 2013). High micro pore volume, on the other hand, indicates that it depicts relatively high internal porosity.

Table 4.2 Surface and Textural properties of catalyst HZSM-5

Parameters	
Surface area	268 m ² /g
Total Pore volume	0.148 cm ³ /g

Average pore diameter	3.2 nm
Meso pore Volume	0.0442 cm ³ /g
Meso pore Area	29.169 m ² /g
Micro pore Volume	0.104 cm ³ /g
Bulk density	0.65g/cm ³

Powder XRD pattern to confirm the crystallinity of HZSM-5 was also performed. As shown in spectra, the characteristic peaks of HZSM-5 were presented at $2\theta=7.8$ and 22.92 which is in the range of $2=7-9^\circ$ and $22-25^\circ$ as reported in literature (Hardenberg et al., 1992; Sang et al., 2004).

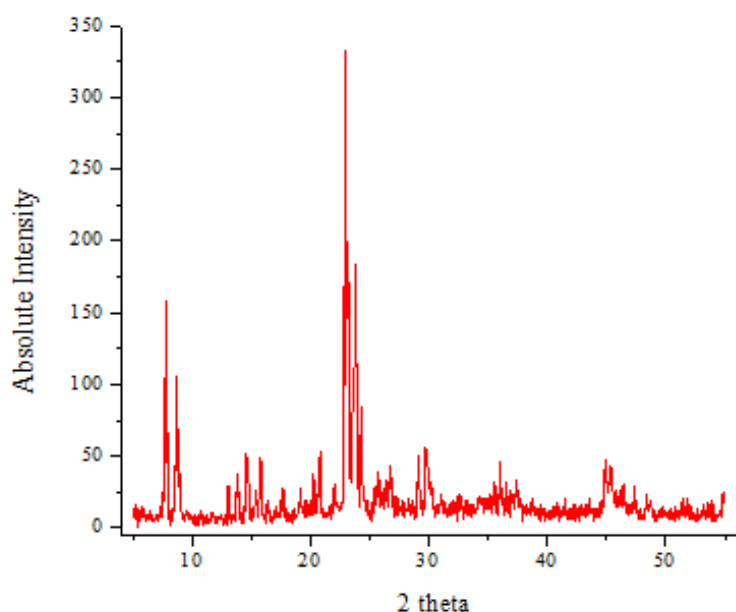


Figure 4.1 XRD Pattern of catalyst HZSM-5

4.3 Effect of feedstock blend ratio on pyrolysis products yield

Product distribution from pyrolysis of Polystyrene and Corn stalk and co pyrolysis of PS and CS at various blend ratios are given in the figure 4.2.

In general, increasing PS quantity in mixture led to increase in oil yield and reduction in char yield owing to the fact that PS is rich in volatile matter and has quite low fixed carbon as compared to Corn stalk. Also as expected, due to low H/C_{eff} and high lignin content of CS, it produced more char. Low gas yield, on the other hand, might be due to

high lignin content of biomass as lignin decomposed slowly at 500°C and released less gas (Brebou et al., 2010). Contrarily, pure PS did not yield any solid product due to no FC and ash content.

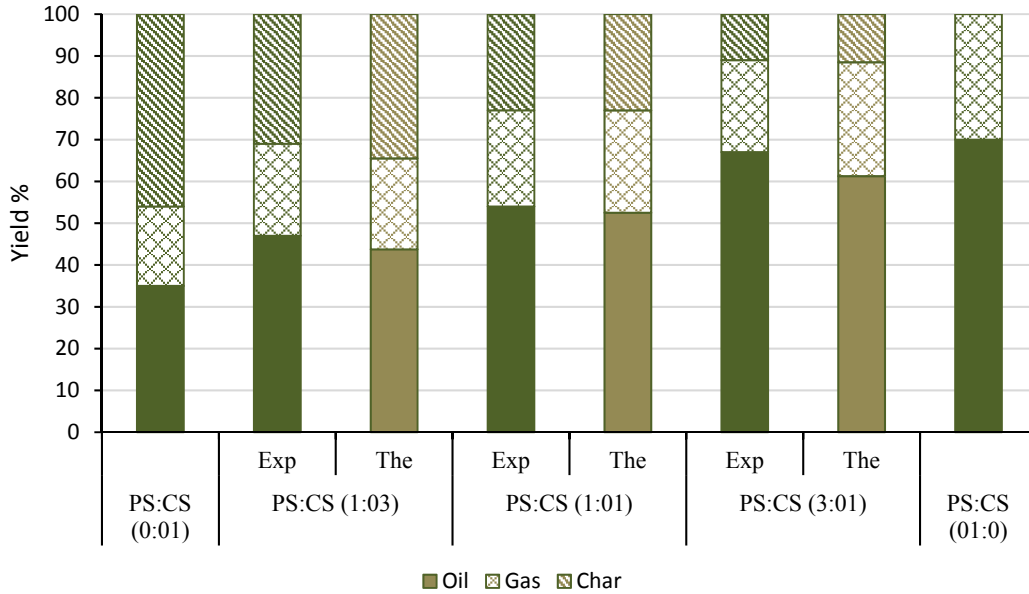


Figure 4.2 Experimental and theoretical pyrolysis product yield of individual feedstock and their blend

Figure 3.3 clearly visualize that addition of PS to CS exhibited positive synergy in case of liquid oil and negative synergy in case of gas and char for all of the selected ratios, which clearly indicates that blending favored bio oil production and opposed the gas and char production. These outcomes can be described by the fact that pyrolysis of PS donate hydrogen and generate free radicals which initiate cross reaction between CS and PS during co pyrolysis. These reactions may lead to breakdown of functional group affixed with cellulose structure of CS which suppress the gas formation with low molecular weight compounds and favors the oil formation with high molecular weight organic compounds (Chen et al., 2016). Further, decrease in char with the increase in PS signifies better degree of conversion (Dewangan et al., 2016) .

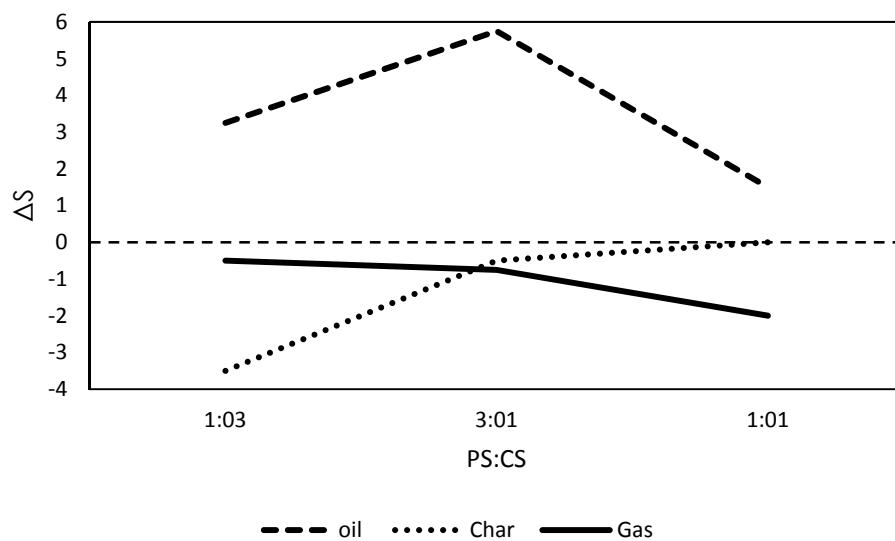


Figure 4.3 Variation of calculated synergistic effect for char, gas and oil as a function of blend ratio

The obvious synergy occurred at 3:1 which is attributed to the fact that PS contains high amount of hydrogen and act as hydrogen donor in hydrogenation reaction. Also the H/C_{eff} of this blend ratio is highest in contrast with other two as shown in figure. Thus PS to CS ratio of 3:1 was selected for catalytic co-pyrolysis.

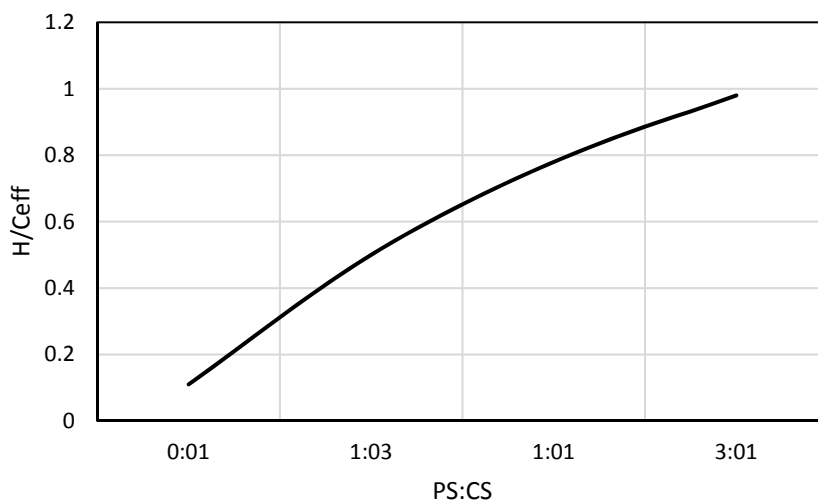


Figure 4.4 Hydrogen to carbon effective ratio as a function of blend ratio

4.4 Effect of In-situ and Ex-situ CFR on pyrolysis products yield

Product distribution from ex-situ and in-situ catalytic co-pyrolysis of Polystyrene and Corn stalk at five different catalyst to feedstock ratio are given in the figure 4.5.

It is observed that increasing catalyst to feedstock ratio (CFR) in ex-situ experiments decreased liquid oil yield from 64.5% to 53% however increased gas yield with the concurrent increase in coke formation. These results can be explained by the fact that augment in catalyst bed height enhances the acidic sites of catalyst and residence time of pyrolysis vapors within the catalyst bed, which leads to secondary reaction favoring gas and coke formation (Zainan et al., 2018). Further, (Balasundram et al., 2018) demonstrated that more quantity of catalyst could hinder the passage of volatiles which in turn transform volatiles via oligomerization and polymerization reactions into coke. Same results were obtained by (Duan et al., 2017) where yield of liquid oil decreased from 51% to 36% with increase in CFR from 0.25 to 1. Char yield, on the other hand, is mainly dependent on pyrolysis conditions (temperature and sweeping gas flow rate) so as the conditions were kept constant in all experiments, the char yield (10.5-11.2%) didn't vary significantly (Fan et al., 2018).

In in-situ experiments, increasing CFR from 0.1 to 0.25 increased liquid oil yield from 65.5% to 66.5% at the expense of decrease in gas yield from 24% to 22.5%. Though, further elevating the ratio declined liquid oil yield to 58% and elevated gas yield to 25.5%. This low liquid yield may be ascribed to higher resistance to heat and mass transfer at high catalyst mass. Also, due to suppressed mass and heat transfer rate, the pyrolysis vapors were exposed to low temperature inside the pores of HZSM-5 which promoted secondary reaction (alkylation reaction) and hence yielded more solid residue (char and coke) (Luo et al., 2016; Wang et al., 2014).

The organic yield decreased in both in situ and ex situ mode as compared to non-catalytic as the deposition of coke deprived the feedstock carbon (Yildiz et al., 2013). Moreover, increase in aqueous phase with catalyst manipulation depicted oxygen removal in the form of water (Naqvi et al., 2014). Additionally, by comparing in-situ product

distribution with that of ex situ, it is concluded that in-situ yielded more Liquid-oil and less gas which is consistent with literature (Fan et al., 2018; Luo et al., 2016).

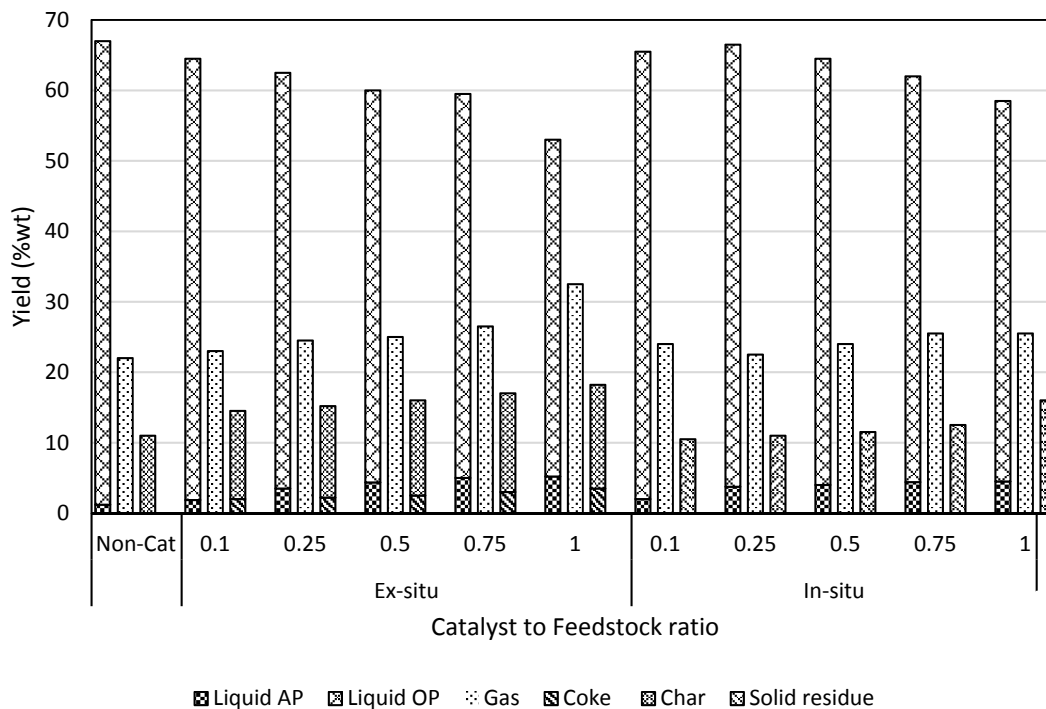


Figure 4.5 Product Yield from Non-catalytic, In-situ and Ex-situ (at various CFR) Catalytic co-pyrolysis

4.5 Liquid oil analysis

4.5.1 GC-MS analysis

The compound distribution from non-catalytic, In-situ and Ex-situ catalytic co pyrolysis at various Catalyst to feedstock ratio is given in the fig 4.6. Obtained pyrolysis oil comprised of complex mixture of organic compounds resulting in identification of several peaks in GC-MS chromatogram. With the intention of making GC-MS analysis results more comprehensive, the identified compounds were categorized into groups conferring their nature and functional groups. These groups include, Mono aromatic hydrocarbons (MAH), Poly aromatic hydrocarbons (PAH), olefins, oxygenates and acids.

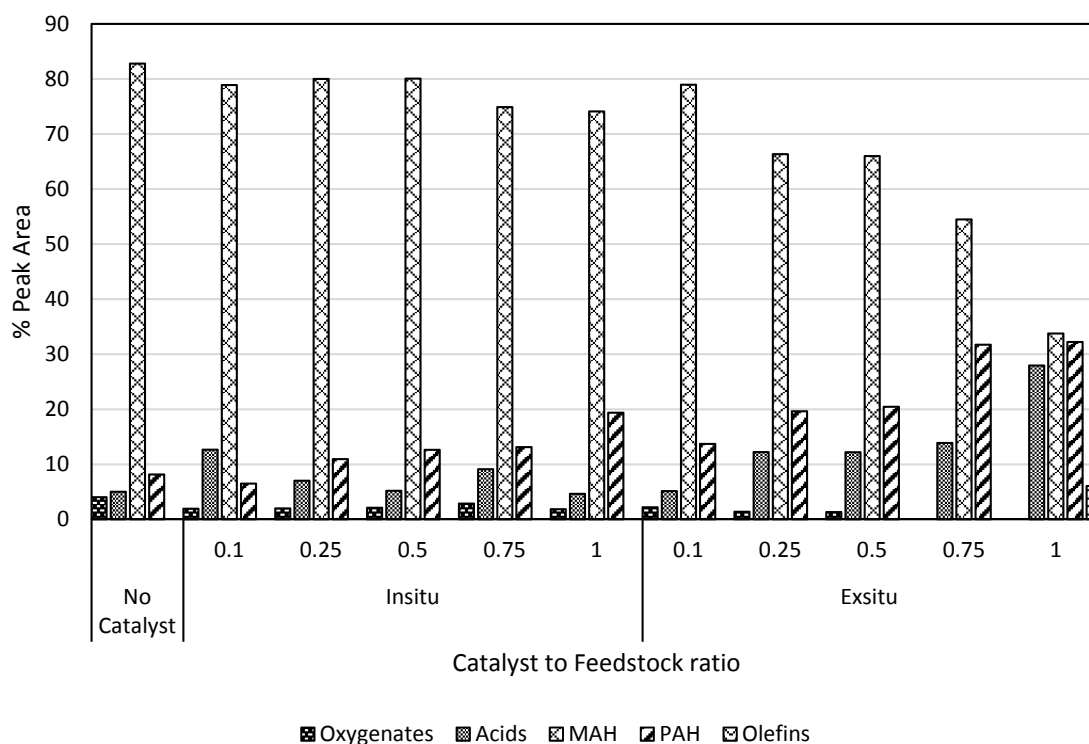


Figure 4.6 GC-MS results for Non catalytic, In-situ and Ex-situ (at various CFR) catalytic co-pyrolysis of CS and PS

Aromatic hydrocarbons were the major products identified with the highest selectivity of styrene in MAH and naphthalene in PAH in all three modes of co-pyrolysis. Keeping in view the comparison between in-situ and ex-situ, it was observed that the MAH peak area during in-situ mode was relatively equal to that of ex-situ at CFR of 0.1 however, with the further augment in catalyst quantity, in-situ generated more MAH than ex-situ mode. Same result was reported by (Kim et al., 2017) who investigated in-situ and ex-situ catalytic co-pyrolysis of biomass and plastic and concluded that in-situ yield more aromatic hydrocarbon as the catalyst is exposed to a more concentrated stream of pyrolysis vapors.

Figure 4.7 and 4.8 presents the selectivity of major mono and poly aromatic hydrocarbons identified with and without catalyst. It is inferred that styrene, a dominant MAH, is de-alkylated to benzene in the presence of HZSM-5 catalyst (Xue et al., 2017).

Hence CFR increment in twain catalytic modes declined styrene formation accompanied by increase in benzene production. Ex-situ CFR of 1 was noticed sufficient enough for complete de-alkylation of styrene into benzene. In contrast, in in-situ co pyrolysis styrene de-alkylation at increasing CFR seemed quite low. This could be ascribed to insufficient contact of pyrolysis vapors with catalyst or due to heat and mass transfer limitations, the pores of HZSM-5 had probably been subjected to low temperature which subsequently resulted in rapid catalyst deactivation, consequently less conversion occurred (Luo et al., 2016).

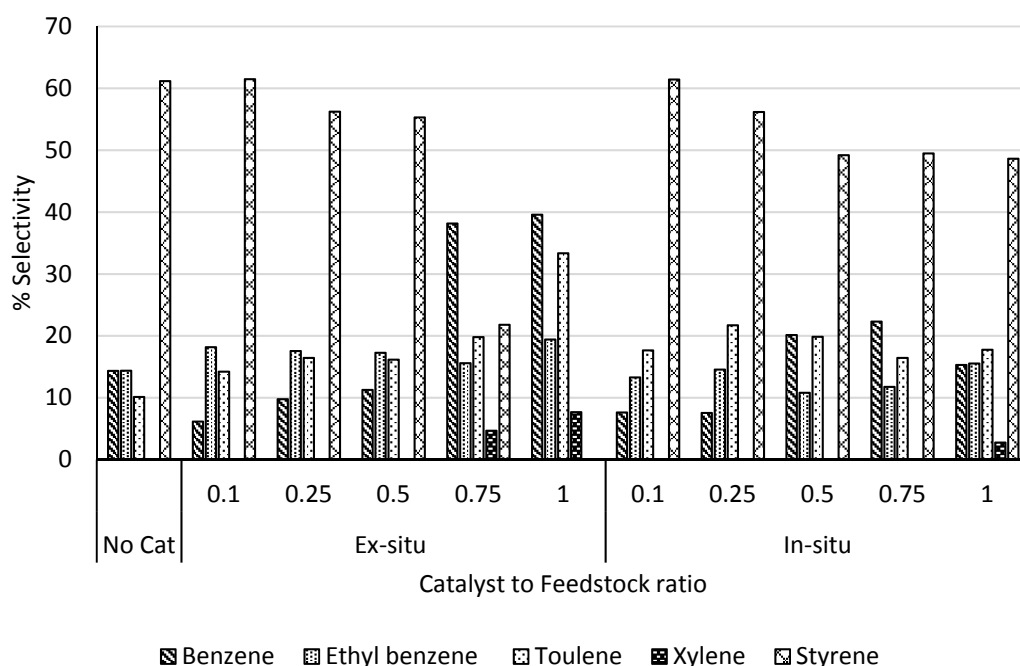


Figure 4.7 Selectivity to MAH

PS being a non-polyolefin contributes less to the formation of olefins (Zhang et al., 2014). However, co pyrolysis of this combination resulted in production of olefin (6.05%) only in ex-situ mode at CFR of 1. This can be attributed to the secondary thermal cracking of pyrolysis vapors prior to catalytic reaction in ex-situ catalytic co-pyrolysis, which leads to conversion of primarily produced small molecule hydrocarbons into olefins (Hu et al., 2017). Wang et al., compared in-situ and ex-situ catalytic upgrading of vapors evolved from pyrolysis of hybrid poplar under identical

reaction conditions and concluded that in-situ yield less olefins (5.4%) than ex-situ (17.4%) as addition of catalyst in the same reactor decelerated the heating rate of biomass which consequently suppressed olefin-based cycle (Wang et al., 2014).

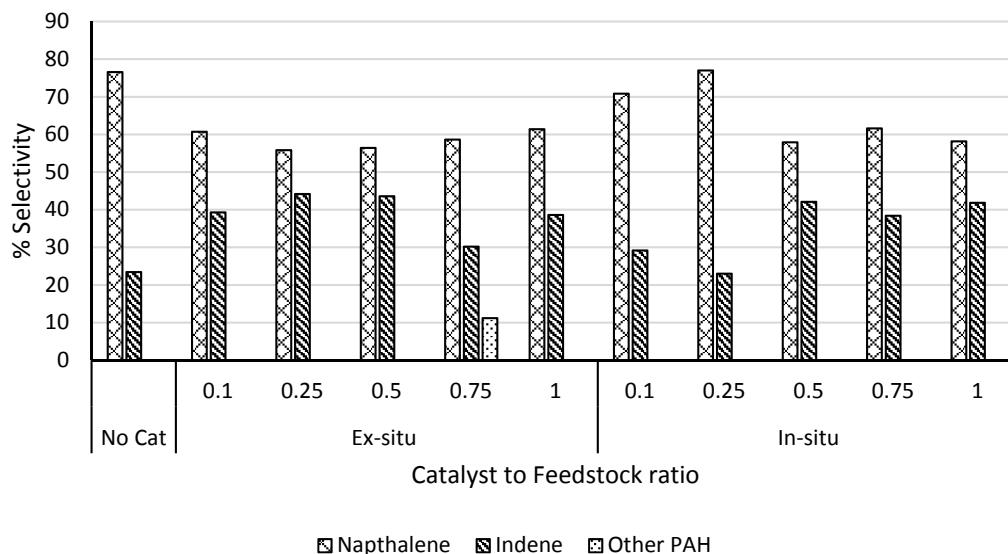


Figure 4.8 Selectivity to PAH

With regard to undesirable compounds, it is indicated that in both catalytic mode of pyrolysis, higher catalyst quantity favored the production of PAH mainly naphthalene which is in good agreement with literature (Ding et al., 2018). The plausible reason for this is augmenting catalyst amount increased availability of active acids sites which successively leads to enhanced internal cyclization of styrene monomers to naphthalene and indane derivatives (Xue et al., 2017).

Besides PAH, acids formation was also observed to be increased with the addition of catalyst which is in accordance with literature (Balasundram et al., 2018; Hu et al., 2017; Naqvi et al., 2014). This is again possibly due to large number of acid sites at higher catalyst to feedstock ratio that adversely produce high contents of acidic compounds. Moreover, % area of oxygenates derived from corn stalk pyrolysis alleviated substantially with catalyst upgrading as volatiles containing oxygenated species enter HZSM-5 pores and undergo several reaction including dehydrogenation,

decarboxylation, decarbonylation, dehydration and oligomerization which in turn result in production of aromatics, CO, CO₂ and water (Ding et al., 2018; Vichaphund et al., 2015; Wang et al., 2018). Peak area of oxygenates were completely eliminated at ex-situ CFR of 0.75 and 1.

In comparison to non-catalytic, it is noteworthy that with the addition of catalyst, total peak area of MAH reduced however, selectivity to benzene, toluene and xylene increased. Maximum selectivity of these compounds obtained were 39.57, 33.35 and 7.67% at CFR of 1 in ex situ and 22.3, 21.72 and 2.75% at CFR of 0.75, 0.25 and 1 respectively in in situ mode. Contrarily, Selectivity to ethyl benzene as compared to non-catalytic increased in ex-situ mode but decreased in in-situ at all CFR which elucidates hydrogenation of styrene monomer into ethyl benzene is suppressed in in-situ (Ojha et al., 2015b). Contrarily, overall selectivity to PAH increased at all CFR except at in-situ CFR of 0.1.

From all of the above discussion, it is concluded that co pyrolysis of corn stalk and polystyrene at blend ratio of 1:3 exhibited better quality without catalyst. Catalyst manipulation with this combination was not able to assist in enhancing the mono aromatic hydrocarbon relative content/peak area which was the formulated hypothesis based on previous reported studies. Thus, non-catalytic co-pyrolysis is selected for further physical analysis.

4.5.2 Physical Analysis

Table 8 represents the physical properties of liquid oil obtained from non-catalytic co pyrolysis of CS and PS. The liquid oil was dark brown in color. Comparison with other transportation fuels indicates that Pour point lie within range and would not cause trouble even in cold regions. As high pour point could produce wax in engine which in turn could make it troublesome in engine startup (Ahmad et al., 2015; Kumar et al., 2014). It is reported that low pour point depicts liquid oil has high aromatic content and low paraffin content which has already been proved by GC-MS in section 4.5.1. Flash

point on the other hand is quite low which may lead to fire hazard during storage and would need extra precaution during handling (Sharuddin et al., 2016).

Table 4.3 Physical properties of optimized liquid oil

Parameters	Liquid oil	Conventional Fuels (Kumar et al., 2014)	
		Diesel	Gasoline
Density at 20 °C (g/cc)	0.9	0.81-0.87	0.72-0.78
Kinematic Viscosity at 40°C (Cst)	4.56	2-5.5	1.17
Specific gravity	0.90	0.82-0.85	0.70
Flash point (°C)	23	53-80	43
Pour point (°C)	<-40C	-40 to -1	-40
HHV MJ/kg	41.80	42-45	42-46

Kinematic viscosity of the fuel manifests spray pattern and atomization behavior in a combustion chamber. Too high and too low viscous oil lead to poor atomization and leakage at the fuel injector respectively which in turn results in poor engine performance (Miandad et al., 2016b). Thus, kinematic viscosity obtained in this study meets with the specifications of diesel so no further upgradation in term of viscosity to use it as vehicle fuel is required.

The produced liquid oil in this study had density of 0.91 g/cc which is in line with many previously reported studies taking different biomass or plastics as feedstock (Ahmad et al., 2015; Shadangi et al., 2014; Uçar et al., 2014). However, this figure is slightly higher than that of commercial fuels. HHV is the most important characteristic of pyrolytic oil. (Saptoadi et al., 2015) Et al., demonstrated that higher HHV fuels are always required in less quantity as compared to low HHV fuel to conduct the same function. HHV of optimized liquid oil direct that energy content is close to conventional fuels however to bring it in range of gasoline or diesel, little blending with diesel/gasoline is required.

The above discussion indicates that obtained liquid oil had qualities close to conventional fuels so it can be used as substitute fuel for use in transportation and gasoline and diesel production after refining or blending with additives.

Chapter 5 CONCLUSION AND RECOMMENDATIONS

Non-catalytic co-pyrolysis of biomass corn stalk and plastic polystyrene was conducted at 500°C with blend ratios of 0:1, 1:3, 1:1, 3:1 and 1:0. It was found that increase in PS proportion led to enhanced liquid oil yield. Based on high liquid product yield, 1:3 was considered for catalytic co-pyrolysis. For catalytic co-pyrolysis a heterogeneous catalyst HZSM-5 with SAR 38 was manipulated. To investigate the effect of catalyst on pyrolysis products yield and composition of liquid oil, catalyst was added in both in-situ and ex-situ mode at five different catalyst to feedstock ratio; 0.1, 0.25, 0.5, 0.75 and 1.0. In either catalyst mode at all CFR, overall liquid oil yield was found to be decreased. GC-MS analysis revealed that oxygenated compounds decreased significantly in comparison to non-catalytic. Among aromatics, styrene exhibited the noteworthy trend. De-alkylation of styrene into benzene with the increase in CFR was noticed. Overall, in-situ mode showed better performance as it contain less PAH, more MAH and less acids and oxygenates as compared to ex-situ which is in line with literature. The observed disparity is attributed to difference in contact time and residence time of pyrolysis vapor with catalyst. However, aromatic yield which was hypothesized to be increased with the addition of catalyst was observed to be declined with this combination of plastic and biomass. Hence, based on high content of mono aromatic hydrocarbons, non-catalytic co-pyrolysis was considered for further physical analysis. Physical analysis showed that liquid oil exhibited properties close to customary petroleum fuel so that it can be used as a substitute of fuel after little blending with conventional fuel.

Even though some properties of the co-pyrolysis liquid oil are closed to customary fuels further upgrading should be made for its application as liquid fuel in engines. Also, catalytic pyrolysis of corn stalk with other plastic more specifically bio-plastic is recommended

REFERENCES

- Abnisa, F., Daud, W. W., & Sahu, J. (2014a). Pyrolysis of mixtures of palm shell and polystyrene: An optional method to produce a high-grade of pyrolysis oil. *Environmental Progress & Sustainable Energy*, 33(3), 1026-1033.
- Abnisa, F., & Wan Daud, W. M. A. (2014b). A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil. *Energy conversion and management*, 87(Supplement C), 71-85. doi:<https://doi.org/10.1016/j.enconman.2014.07.007>
- Administration, U. S. E. I. (2017). International Energy Outlook
- Ahmad, I., Khan, M. I., Ishaq, M., Khan, H., Gul, K., & Ahmad, W. (2013). Catalytic efficiency of some novel nanostructured heterogeneous solid catalysts in pyrolysis of HDPE. *Polymer degradation and stability*, 98(12), 2512-2519.
- Ahmad, I., Khan, M. I., Khan, H., Ishaq, M., Tariq, R., Gul, K., et al. (2015). Pyrolysis study of polypropylene and polyethylene into premium oil products. *International journal of green energy*, 12(7), 663-671.
- Aho, A., Kumar, N., Eränen, K., Salmi, T., Hupa, M., & Murzin, D. Y. (2008). Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure. *Fuel*, 87(12), 2493-2501. doi:<https://doi.org/10.1016/j.fuel.2008.02.015>
- Alagu, R., Sundaram, E. G., & Natarajan, E. (2015). Thermal and catalytic slow pyrolysis of Calophyllum inophyllum fruit shell. *Bioresource Technology*, 193, 463-468.
- Agency, I. E. (2013). *Resource to Reserves*. Retrieved from
- Artetxe, M., Lopez, G., Amutio, M., Elordi, G., Bilbao, J., & Olazar, M. (2013). Cracking of high density polyethylene pyrolysis waxes on HZSM-5 catalysts of different acidity. *Industrial & Engineering Chemistry Research*, 52(31), 10637-10645.
- Ateş, F., Pütün, A. E., & Pütün, E. (2006). Pyrolysis of two different biomass samples in a fixed-bed reactor combined with two different catalysts. *Fuel*, 85(12-13), 1851-1859.
- Balasundram, V., Ibrahim, N., Kasmani, R. M., Isha, R., Hamid, M. K. A., Hasbullah, H., et al. (2018). Catalytic upgrading of sugarcane bagasse pyrolysis vapours over rare earth metal (Ce) loaded HZSM-5: Effect of catalyst to biomass ratio on the organic compounds in pyrolysis oil. *Applied Energy*, 220, 787-799.
- Beis, S. H., Onay, Ö., & Koçkar, Ö. M. (2002). Fixed-bed pyrolysis of safflower seed: influence of pyrolysis parameters on product yields and compositions. *Renewable Energy*, 26(1), 21-32. doi:[https://doi.org/10.1016/S0960-1481\(01\)00109-4](https://doi.org/10.1016/S0960-1481(01)00109-4)
- Brebu, M., Ucar, S., Vasile, C., & Yanik, J. (2010). Co-pyrolysis of pine cone with synthetic polymers. *Fuel*, 89(8), 1911-1918.
- Bridgeman, T. G., Jones, J. M., Williams, A., & Waldron, D. J. (2010). An investigation of the grindability of two torrefied energy crops. *Fuel*, 89(12), 3911-3918. doi:<https://doi.org/10.1016/j.fuel.2010.06.043>
- Bridgwater, A. (1996). Production of high grade fuels and chemicals from catalytic pyrolysis of biomass. *Catalysis today*, 29(1-4), 285-295.
- Bulushev, D. A., & Ross, J. R. (2011). Catalysis for conversion of biomass to fuels via pyrolysis and gasification: a review. *Catalysis Today*, 171(1), 1-13.

- Capunitan, J. A., & Capareda, S. C. (2012). Assessing the potential for biofuel production of corn stover pyrolysis using a pressurized batch reactor. *Fuel*, *95*, 563-572. doi:<https://doi.org/10.1016/j.fuel.2011.12.029>
- Carlson, T. R., Jae, J., Lin, Y.-C., Tompsett, G. A., & Huber, G. W. (2010). Catalytic fast pyrolysis of glucose with HZSM-5: The combined homogeneous and heterogeneous reactions. *Journal of Catalysis*, *270*(1), 110-124. doi:<https://doi.org/10.1016/j.jcat.2009.12.013>
- Çepelioğullar, Ö., & Pütün, A. E. (2014). Products characterization study of a slow pyrolysis of biomass-plastic mixtures in a fixed-bed reactor. *Journal of analytical and applied pyrolysis*, *110*, 363-374.
- Chattopadhyay, J., Pathak, T., Srivastava, R., & Singh, A. (2016). Catalytic co-pyrolysis of paper biomass and plastic mixtures (HDPE (high density polyethylene), PP (polypropylene) and PET (polyethylene terephthalate)) and product analysis. *Energy*, *103*, 513-521.
- Chaudhry, M. F. (2010). *Evolution of plastics Industry in Pakistan*.
- Chen, J., Liu, C., & Wu, S.-b. (2015). Catalytic fast pyrolysis of Alcell lignin with nano-NiO. *BioResources*, *11*(1), 663-673.
- Chen, W., Shi, S., Zhang, J., Chen, M., & Zhou, X. (2016). Co-pyrolysis of waste newspaper with high-density polyethylene: synergistic effect and oil characterization. *Energy conversion and management*, *112*, 41-48.
- Cheng, S., Wei, L., Zhao, X., Huang, Y., Raynie, D., Qiu, C., et al. (2015). *Directly catalytic upgrading bio-oil vapor produced by prairie cordgrass pyrolysis over Ni/HZSM-5 using a two stage reactor* (Vol. 3).
- Chin, B. L. F., Yusup, S., Al Shoaibi, A., Kannan, P., Srinivasakannan, C., & Sulaiman, S. A. (2014). Kinetic studies of co-pyrolysis of rubber seed shell with high density polyethylene. *Energy conversion and management*, *87*, 746-753.
- Das, P., & Ganesh, A. (2003). Bio-oil from pyrolysis of cashew nut shell—a near fuel. *Biomass and Bioenergy*, *25*(1), 113-117. doi:[https://doi.org/10.1016/S0961-9534\(02\)00182-4](https://doi.org/10.1016/S0961-9534(02)00182-4)
- de Miguel Mercader, F., Groeneveld, M. J., Kersten, S. R., Geantet, C., Toussaint, G., Way, N. W., et al. (2011). Hydrodeoxygenation of pyrolysis oil fractions: process understanding and quality assessment through co-processing in refinery units. *Energy & environmental science*, *4*(3), 985-997.
- Demiral, İ., & Şensöz, S. (2006). Fixed-Bed Pyrolysis of Hazelnut (*Corylus Avellana* L.) Bagasse: Influence of Pyrolysis Parameters on Product Yields. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, *28*(12), 1149-1158. doi:10.1080/009083190966126
- Demirbas, M. F. (2010). Characterization of Bio-oils from Spruce Wood (*Picea orientalis* L.) via Pyrolysis. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, *32*(10), 909-916. doi:10.1080/15567030903059970
- Dewangan, A., Pradhan, D., & Singh, R. (2016). Co-pyrolysis of sugarcane bagasse and low-density polyethylene: Influence of plastic on pyrolysis product yield. *Fuel*, *185*, 508-516.
- Dickerson, T., & Soria, J. (2013). Catalytic fast pyrolysis: a review. *Energies*, *6*(1), 514-538.
- Ding, K., Zhong, Z., Wang, J., Zhang, B., Fan, L., Liu, S., et al. (2018). Improving hydrocarbon yield from catalytic fast co-pyrolysis of hemicellulose and plastic in the dual-catalyst bed of CaO and HZSM-5. *Bioresource Technology*, *261*, 86-92.

- Ding, T., Li, S., Xie, J., Song, W., Yao, J., & Lin, W. (2012). Rapid pyrolysis of wheat straw in a bench-scale circulating fluidized-bed downer reactor. *Chemical Engineering & Technology*, 35(12), 2170-2176.
- Du, S., Sun, Y., Gamliel, D. P., Valla, J. A., & Bollas, G. M. (2014). Catalytic pyrolysis of miscanthus× giganteus in a spouted bed reactor. *Bioresource Technology*, 169, 188-197.
- Duan, D., Wang, Y., Dai, L., Ruan, R., Zhao, Y., Fan, L., et al. (2017). Ex-situ catalytic co-pyrolysis of lignin and polypropylene to upgrade bio-oil quality by microwave heating. *Bioresource Technology*, 241, 207-213.
- Duman, G., Okutucu, C., Ucar, S., Stahl, R., & Yanik, J. (2011). The slow and fast pyrolysis of cherry seed. *Bioresource Technology*, 102(2), 1869-1878. doi:<https://doi.org/10.1016/j.biortech.2010.07.051>
- Durange, J. A., Santos, M. R., Pereira, M. M., Fernandes Jr, L. A., Souza, M. N., Mendes, A. N., et al. (2013). Physicochemical properties of pyrolysis bio-oil from sugarcane straw and sugarcane in Natura. *Journal of Biomaterials and Nanobiotechnology*, 4(02), 10.
- El Mogahzy, Y. E. (2009). 13 - Development of technical textile products: materials and applications. In Y. E. El Mogahzy (Ed.), *Engineering Textiles* (pp. 398-434): Woodhead Publishing.
- Elliott, D., Beckman, D., Bridgwater, A., Diebold, J., Gevert, S., & Solantausta, Y. (1991). Developments in direct thermochemical liquefaction of biomass: 1983-1990. *Energy & Fuels*, 5(3), 399-410.
- Elsayed, I., & Eseyin, A. (2016). Production high yields of aromatic hydrocarbons through catalytic fast pyrolysis of torrefied wood and polystyrene. *Fuel*, 174, 317-324.
- Fan, L., Chen, P., Zhou, N., Liu, S., Zhang, Y., Liu, Y., et al. (2018). In-situ and ex-situ catalytic upgrading of vapors from microwave-assisted pyrolysis of lignin. *Bioresource Technology*, 247, 851-858.
- Foster, A. J., Jae, J., Cheng, Y.-T., Huber, G. W., & Lobo, R. F. (2012). Optimizing the aromatic yield and distribution from catalytic fast pyrolysis of biomass over ZSM-5. *Applied Catalysis A: General*, 423, 154-161.
- French, R., & Czernik, S. (2010). Catalytic pyrolysis of biomass for biofuels production. *Fuel Processing Technology*, 91(1), 25-32.
- Gerçel, H. F. (2002). The Effect of a Sweeping Gas Flow Rate on the Fast Pyrolysis of Biomass. *Energy Sources*, 24(7), 633-642. doi:10.1080/00908312.2002.11877438
- Gollakota, A. R., Reddy, M., Subramanyam, M. D., & Kishore, N. (2016). A review on the upgradation techniques of pyrolysis oil. *Renewable and Sustainable Energy Reviews*, 58, 1543-1568.
- González-Borja, M. Á., & Resasco, D. E. (2011). Anisole and guaiacol hydrodeoxygenation over monolithic Pt–Sn catalysts. *Energy & Fuels*, 25(9), 4155-4162.
- Gulab, H., Hussain, K., Malik, S., Hussain, Z., & Shah, Z. (2016). Catalytic co-pyrolysis of Eichhornia Crassipes biomass and polyethylene using waste Fe and CaCO₃ catalysts. *International Journal of Energy Research*, 40(7), 940-951.
- Gunasee, S. D., Danon, B., Görgens, J. F., & Mohee, R. (2017). Co-pyrolysis of LDPE and cellulose: Synergies during devolatilization and condensation. *Journal of analytical and applied pyrolysis*, 126, 307-314.
- Guo, M., & Bi, J. (2015). Pyrolysis characteristics of corn stalk with solid heat carrier. *BioResources*, 10(3), 3839-3851.

- Hardenberg, T., Mertens, L., Mesman, P., Muller, H., & Nicolaidis, C. (1992). A catalytic method for the quantitative evaluation of crystallinities of ZSM-5 zeolite preparations. *Zeolites*, 12(6), 685-689.
- Hassan, H., Lim, J., & Hameed, B. (2016). Recent progress on biomass co-pyrolysis conversion into high-quality bio-oil. *Bioresource Technology*, 221, 645-655.
- Hu, C., Xiao, R., & Zhang, H. (2017). Ex-situ catalytic fast pyrolysis of biomass over HZSM-5 in a two-stage fluidized-bed/fixed-bed combination reactor. *Bioresource Technology*, 243, 1133-1140.
- Iliopoulou, E., Stefanidis, S., Kalogiannis, K., Psarras, A., Delimitis, A., Triantafyllidis, K., et al. (2014). Pilot-scale validation of Co-ZSM-5 catalyst performance in the catalytic upgrading of biomass pyrolysis vapours. *Green Chemistry*, 16(2), 662-674.
- Iliopoulou, E. F., Stefanidis, S., Kalogiannis, K., Delimitis, A., Lappas, A., & Triantafyllidis, K. (2012). Catalytic upgrading of biomass pyrolysis vapors using transition metal-modified ZSM-5 zeolite. *Applied Catalysis B: Environmental*, 127, 281-290.
- Islam, M. R., Nabi, M. N., & Islam, M. N. (2001). *Characterization of biomass solid waste for liquid fuel production*. Paper presented at the Proc. of.
- Jae, J., Tompsett, G. A., Foster, A. J., Hammond, K. D., Auerbach, S. M., Lobo, R. F., et al. (2011). Investigation into the shape selectivity of zeolite catalysts for biomass conversion. *Journal of Catalysis*, 279(2), 257-268. doi:<https://doi.org/10.1016/j.jcat.2011.01.019>
- Ji-lu, Z. (2007). Bio-oil from fast pyrolysis of rice husk: Yields and related properties and improvement of the pyrolysis system. *Journal of analytical and applied pyrolysis*, 80(1), 30-35. doi:<https://doi.org/10.1016/j.jaap.2006.12.030>
- Kabir, G., & Hameed, B. (2017). Recent progress on catalytic pyrolysis of lignocellulosic biomass to high-grade bio-oil and bio-chemicals. *Renewable and Sustainable Energy Reviews*, 70, 945-967.
- Kan, T., Strezov, V., & Evans, T. J. (2016). Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renewable and Sustainable Energy Reviews*, 57, 1126-1140. doi:<https://doi.org/10.1016/j.rser.2015.12.185>
- Kim, B.-S., Kim, Y.-M., Jae, J., Watanabe, C., Kim, S., Jung, S.-C., et al. (2015). Pyrolysis and catalytic upgrading of Citrus unshiu peel. *Bioresource Technology*, 194, 312-319.
- Kim, Y.-M., Jae, J., Kim, B.-S., Hong, Y., Jung, S.-C., & Park, Y.-K. (2017). Catalytic co-pyrolysis of torrefied yellow poplar and high-density polyethylene using microporous HZSM-5 and mesoporous Al-MCM-41 catalysts. *Energy conversion and management*, 149, 966-973. doi:<https://doi.org/10.1016/j.enconman.2017.04.033>
- Kumar, S., & Singh, R. (2014). Optimization of process parameters by response surface methodology (RSM) for catalytic pyrolysis of waste high-density polyethylene to liquid fuel. *Journal of Environmental Chemical Engineering*, 2(1), 115-122.
- Lee, H. W., Choi, S. J., Jeon, J.-K., Park, S. H., & Park, Y.-K. (2014a). Catalytic Co-Pyrolysis of Waste Particle Board and Polypropylene Over Nanoporous Al-MCM-41 Catalysts. *Journal of nanoscience and nanotechnology*, 14(11), 8489-8494.
- Lee, H. W., Choi, S. J., Park, S. H., Jeon, J.-K., Jung, S.-C., Joo, S. H., et al. (2014b). Catalytic conversion of *Laminaria japonica* over microporous zeolites. *Energy*, 66, 2-6.
- Li, J., Li, X., Zhou, G., Wang, W., Wang, C., Komarneni, S., et al. (2014). Catalytic fast pyrolysis of biomass with mesoporous ZSM-5 zeolites prepared by desilication with NaOH solutions. *Applied Catalysis A: General*, 470, 115-122.

- Li, X., Li, J., Zhou, G., Feng, Y., Wang, Y., Yu, G., et al. (2014). Enhancing the production of renewable petrochemicals by co-feeding of biomass with plastics in catalytic fast pyrolysis with ZSM-5 zeolites. *Applied Catalysis A: General*, *481*, 173-182.
- Lu, Q., Zhang, Z.-F., Dong, C.-Q., & Zhu, X.-F. (2010). Catalytic upgrading of biomass fast pyrolysis vapors with nano metal oxides: an analytical Py-GC/MS study. *Energies*, *3*(11), 1805-1820.
- Luo, G., & Resende, F. L. (2016). In-situ and ex-situ upgrading of pyrolysis vapors from beetle-killed trees. *Fuel*, *166*, 367-375.
- Lv, G.-j., Wu, S.-b., & Lou, R. (2010). Kinetic study for the thermal decomposition of hemicellulose isolated from corn stalk. *BioResources*, *5*(2), 1281-1291.
- Martínez, J. D., Veses, A., Mastral, A. M., Murillo, R., Navarro, M. V., Puy, N., et al. (2014). Co-pyrolysis of biomass with waste tyres: upgrading of liquid bio-fuel. *Fuel Processing Technology*, *119*, 263-271.
- Miandad, R., Barakat, M., Aburizaiza, A. S., Rehan, M., & Nizami, A. (2016a). Catalytic pyrolysis of plastic waste: a review. *Process Safety and Environmental Protection*, *102*, 822-838.
- Miandad, R., Nizami, A., Rehan, M., Barakat, M., Khan, M., Mustafa, A., et al. (2016b). Influence of temperature and reaction time on the conversion of polystyrene waste to pyrolysis liquid oil. *Waste management*, *58*, 250-259.
- Naqvi, S. R., Uemura, Y., & Yusup, S. B. (2014). Catalytic pyrolysis of paddy husk in a drop type pyrolyzer for bio-oil production: The role of temperature and catalyst. *Journal of analytical and applied pyrolysis*, *106*, 57-62.
- Neupane, S., Adhikari, S., Wang, Z., Ragauskas, A. J., & Pu, Y. (2015). Effect of torrefaction on biomass structure and hydrocarbon production from fast pyrolysis. *Green Chemistry*, *17*(4), 2406-2417. doi:10.1039/C4GC02383H
- Ojha, D. K., & Vinu, R. (2015a). Fast co-pyrolysis of cellulose and polypropylene using Py-GC/MS and Py-FT-IR. *RSC Advances*, *5*(82), 66861-66870.
- Ojha, D. K., & Vinu, R. (2015b). Resource recovery via catalytic fast pyrolysis of polystyrene using zeolites. *Journal of analytical and applied pyrolysis*, *113*, 349-359.
- Önal, E., Uzun, B. B., & Pütün, A. E. (2014). Bio-oil production via co-pyrolysis of almond shell as biomass and high density polyethylene. *Energy conversion and management*, *78*, 704-710.
- Onay, O., & Kockar, O. M. (2003). Slow, fast and flash pyrolysis of rapeseed. *Renewable Energy*, *28*(15), 2417-2433. doi:[https://doi.org/10.1016/S0960-1481\(03\)00137-X](https://doi.org/10.1016/S0960-1481(03)00137-X)
- Paradela, F., Pinto, F., Gulyurtlu, I., Cabrita, I., & Lapa, N. (2009a). Study of the co-pyrolysis of biomass and plastic wastes. *Clean Technologies and Environmental Policy*, *11*(1), 115-122.
- Paradela, F., Pinto, F., Ramos, A. M., Gulyurtlu, I., & Cabrita, I. (2009b). Study of the slow batch pyrolysis of mixtures of plastics, tyres and forestry biomass wastes. *Journal of analytical and applied pyrolysis*, *85*(1-2), 392-398.
- Pütün, A. E., Önal, E., Uzun, B. B., & Özbay, N. (2007). Comparison between the "slow" and "fast" pyrolysis of tobacco residue. *Industrial Crops and Products*, *26*(3), 307-314. doi:<https://doi.org/10.1016/j.indcrop.2007.03.011>
- Pütün, A. E., Özbay, N., Önal, E. P., & Pütün, E. (2005). Fixed-bed pyrolysis of cotton stalk for liquid and solid products. *Fuel Processing Technology*, *86*(11), 1207-1219. doi:<https://doi.org/10.1016/j.fuproc.2004.12.006>

- Pütün, E. (2010). Catalytic pyrolysis of biomass: Effects of pyrolysis temperature, sweeping gas flow rate and MgO catalyst. *Energy*, 35(7), 2761-2766. doi:<https://doi.org/10.1016/j.energy.2010.02.024>
- Pütün, E., Uzun, B. B., & Pütün, A. E. (2006). Fixed-bed catalytic pyrolysis of cotton-seed cake: Effects of pyrolysis temperature, natural zeolite content and sweeping gas flow rate. *Bioresource Technology*, 97(5), 701-710. doi:<https://doi.org/10.1016/j.biortech.2005.04.005>
- Ratnasari, D. K., Nahil, M. A., & Williams, P. T. (2017). Catalytic pyrolysis of waste plastics using staged catalysis for production of gasoline range hydrocarbon oils. *Journal of analytical and applied pyrolysis*, 124, 631-637.
- Ren, S., Lei, H., Wang, L., Bu, Q., Chen, S., Wu, J., et al. (2013). The effects of torrefaction on compositions of bio-oil and syngas from biomass pyrolysis by microwave heating. *Bioresource Technology*, 135, 659-664. doi:<https://doi.org/10.1016/j.biortech.2012.06.091>
- Saeed, M., Irshad, A., Sattar, H., Andrews, G., Phylaktou, H., & Gibbs, B. (2015). *Agricultural waste biomass energy potential in Pakistan*. Paper presented at the Proceedings of the International Conference held in Shanghai, PR China.
- Sang, S., Chang, F., Liu, Z., He, C., He, Y., & Xu, L. (2004). Difference of ZSM-5 zeolites synthesized with various templates. *Catalysis Today*, 93, 729-734.
- Saptoadi, H., & Pratama, N. N. (2015). Utilization of plastics waste oil as partial substitute for kerosene in pressurized cookstoves. *International Journal of Environmental Science and Development*, 6(5), 363.
- Şensöz, S., & Kaynar, İ. (2006). Bio-oil production from soybean (*Glycine max* L.); fuel properties of Bio-oil. *Industrial Crops and Products*, 23(1), 99-105. doi:<https://doi.org/10.1016/j.indcrop.2005.04.005>
- Shadangi, K. P., & Mohanty, K. (2014). Effect of Co-pyrolysis of mahua seed and waste polystyrene on quality of liquid fuel. *Journal of Renewable and Sustainable Energy*, 6(5), 053142.
- Shadangi, K. P., & Mohanty, K. (2015). Co-pyrolysis of Karanja and Niger seeds with waste polystyrene to produce liquid fuel. *Fuel*, 153, 492-498.
- Shah, A., Darr, M. J., Dalluge, D., Medic, D., Webster, K., & Brown, R. C. (2012). Physicochemical properties of bio-oil and biochar produced by fast pyrolysis of stored single-pass corn stover and cobs. *Bioresource Technology*, 125, 348-352. doi:<https://doi.org/10.1016/j.biortech.2012.09.061>
- Sharuddin, S. D. A., Abnisa, F., Daud, W. M. A. W., & Aroua, M. K. (2016). A review on pyrolysis of plastic wastes. *Energy conversion and management*, 115, 308-326.
- Stefanidis, S., Kalogiannis, K., Iliopoulou, E., Lappas, A., & Pilavachi, P. (2011). In-situ upgrading of biomass pyrolysis vapors: catalyst screening on a fixed bed reactor. *Bioresource Technology*, 102(17), 8261-8267.
- Uçar, S., & Karagöz, S. (2014). Co-pyrolysis of pine nut shells with scrap tires. *Fuel*, 137, 85-93.
- Uzun, B. B., Pütün, A. E., & Pütün, E. (2007). Composition of products obtained via fast pyrolysis of olive-oil residue: Effect of pyrolysis temperature. *Journal of analytical and applied pyrolysis*, 79(1), 147-153. doi:<https://doi.org/10.1016/j.jaap.2006.12.005>
- Uzun, B. B., & Sarioğlu, N. (2009). Rapid and catalytic pyrolysis of corn stalks. *Fuel Processing Technology*, 90(5), 705-716.

- Vamvuka, D., Troulinos, S., & Kastanaki, E. (2006). The effect of mineral matter on the physical and chemical activation of low rank coal and biomass materials. *Fuel*, *85*(12-13), 1763-1771.
- Van der Stelt, M., Gerhauser, H., Kiel, J., & Ptasinski, K. (2011). Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass and bioenergy*, *35*(9), 3748-3762.
- Vichaphund, S., Aht-ong, D., Sricharoenchaikul, V., & Atong, D. (2015). Production of aromatic compounds from catalytic fast pyrolysis of *Jatropha* residues using metal/HZSM-5 prepared by ion-exchange and impregnation methods. *Renewable Energy*, *79*, 28-37.
- Wang, K., Johnston, P. A., & Brown, R. C. (2014). Comparison of in-situ and ex-situ catalytic pyrolysis in a micro-reactor system. *Bioresource Technology*, *173*, 124-131.
- Wang, K., Zheng, Y., Zhu, X., Brewer, C. E., & Brown, R. C. (2017). Ex-situ catalytic pyrolysis of wastewater sewage sludge—A micro-pyrolysis study. *Bioresource Technology*, *232*, 229-234.
- Wang, Y., Wu, Q., Duan, D., Ruan, R., Liu, Y., Dai, L., et al. (2018). Ex-situ catalytic upgrading of vapors from fast microwave-assisted co-pyrolysis of *Chromolaena odorata* and soybean soapstock. *Bioresource Technology*, *261*, 306-312.
- Wildschut, J., Mahfud, F. H., Venderbosch, R. H., & Heeres, H. J. (2009). Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. *Industrial & Engineering Chemistry Research*, *48*(23), 10324-10334.
- Wildschut, J., Melian-Cabrera, I., & Heeres, H. (2010). Catalyst studies on the hydrotreatment of fast pyrolysis oil. *Applied Catalysis B: Environmental*, *99*(1-2), 298-306.
- Williams, E. A., & Williams, P. T. (1997). The pyrolysis of individual plastics and a plastic mixture in a fixed bed reactor. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental AND Clean Technology*, *70*(1), 9-20.
- Williams, P. T., & Nugranad, N. (2000). Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks. *Energy*, *25*(6), 493-513.
- Wu, J., Chen, T., Luo, X., Han, D., Wang, Z., & Wu, J. (2014). TG/FTIR analysis on co-pyrolysis behavior of PE, PVC and PS. *Waste management*, *34*(3), 676-682.
- Xue, Y., Johnston, P., & Bai, X. (2017). Effect of catalyst contact mode and gas atmosphere during catalytic pyrolysis of waste plastics. *Energy conversion and management*, *142*, 441-451.
- Yildiz, G., Pronk, M., Djokic, M., van Geem, K. M., Ronsse, F., van Duren, R., et al. (2013). Validation of a new set-up for continuous catalytic fast pyrolysis of biomass coupled with vapour phase upgrading. *Journal of analytical and applied pyrolysis*, *103*, 343-351.
- Yin, C. (2012). Microwave-assisted pyrolysis of biomass for liquid biofuels production. *Bioresource Technology*, *120*, 273-284.
- Zainan, N. H., Srivatsa, S. C., Li, F., & Bhattacharya, S. (2018). Quality of bio-oil from catalytic pyrolysis of microalgae *Chlorella vulgaris*. *Fuel*, *223*, 12-19.
- Zhang, B., Zhong, Z., Ding, K., & Song, Z. (2015a). Production of aromatic hydrocarbons from catalytic co-pyrolysis of biomass and high density polyethylene: analytical Py-GC/MS study. *Fuel*, *139*, 622-628.
- Zhang, B., Zhong, Z., Min, M., Ding, K., Xie, Q., & Ruan, R. (2015b). Catalytic fast co-pyrolysis of biomass and food waste to produce aromatics: Analytical Py-GC/MS study. *Bioresource Technology*, *189*, 30-35.

- Zhang, H., Cheng, Y.-T., Vispute, T. P., Xiao, R., & Huber, G. W. (2011). Catalytic conversion of biomass-derived feedstocks into olefins and aromatics with ZSM-5: the hydrogen to carbon effective ratio. *Energy & environmental science*, 4(6), 2297-2307.
- Zhang, H., Nie, J., Xiao, R., Jin, B., Dong, C., & Xiao, G. (2014). Catalytic co-pyrolysis of biomass and different plastics (polyethylene, polypropylene, and polystyrene) to improve hydrocarbon yield in a fluidized-bed reactor. *Energy & Fuels*, 28(3), 1940-1947.
- Zhang, H., Xiao, R., Huang, H., & Xiao, G. (2009). Comparison of non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor. *Bioresource Technology*, 100(3), 1428-1434.
- Zhu, X., Lobban, L. L., Mallinson, R. G., & Resasco, D. E. (2010). Tailoring the mesopore structure of HZSM-5 to control product distribution in the conversion of propanal. *Journal of Catalysis*, 271(1), 88-98. doi:<https://doi.org/10.1016/j.jcat.2010.02.004>