UPGRADING OF BIO-OIL BY INCORPORATING METHANE IN FAST PYROLYSIS OF MUNICIPAL SOLID WASTE (MSW) AND BIOMASS

By

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Abstract:

Fast pyrolysis is promising technology that produces liquid fuels (known as bio-oil) through thermal decomposition of biomass or municipal solid waste in absence of oxygen. Bio-oil has potential application in the transportation sector. However, because of its unwanted properties (such high oxygen, acidic, and low energy) that are detrimental to current infrastructures, bio-oil can be used directly without being upgraded. This study was focused on addressing these undesirable properties of bio-oil by introducing methane over catalysts (HZSM-5 and MoZn/HZSM-5) during fast pyrolysis. A fixed bed and pyroprobe reactors were employed to investigate effects of methane, temperature and catalyst on the weight yield, energy recovery, chemical composition and aromatic hydrocarbons yield of bio-oil from eastern red cedar and municipal solid waste. In chapter II, eastern red cedar pyrolysis experiments were carried out using both reactors under methane and helium over both catalysts at 650 and 750℃. Chemical composition and energy content were analyzed in gas chromatography/mass spectrometry and bomb calorimeter, respectively. The maximum bio-oil yield of 53.4 wt% and energy content of 10.2 MJ/kg achieved when methane was used over MoZn/HZSM-5 at 650℃. This indicated that introduction of methane in fast catalytic pyrolysis of eastern red cedar improved the quality of bio-oil. MoZn/HZSM-5 improved aromatics hydrocarbon yield and a maximum of 56.8 area% was achieved at 750℃ under methane. Both catalysts considerably reduced oxygenated compounds at both temperatures of 650 and 750℃. This showed that deoxygenation can be achieved in presence of methane over MoZn/HZSM-5. In chapter III, a pyroprobe reactor was employed to conduct a pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) analysis of pyrolysis of municipal solid waste over both catalysts at 550, 650 and 750℃. Carbon yield of aromatics hydrocarbons was increased from the maximum of 39.8% in non-catalytic to the highest yield of 56.8% under methane over MoZn/HZSM-5 at 650℃. This showed that methane, a major component of natural gas which is abundant in natural gas reservoirs, is potential hydrogen donor for upgrading bio-oil during fast pyrolysis.

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CHAPTER I

1 INTRODUCTION

As the world's population grows with ever expanding industrialization, urbanization, and development, the consumption of transport liquid fuels from non-renewable fossil reserves continues to increase rapidly. This raises concerns about depleting fossil fuels together with its negative impact on atmosphere due to the release of underground carbon into the atmosphere as carbon dioxide and methane. These concerns are driving research institutions, academicians, scientists and other concerned societies toward the search for alternative renewable sources of power and transportation liquid fuels. Carbonaceous biomass and municipal solid wastes (MSW) are two abundant but underutilized resources that can potentially be converted into transportation liquid fuels. MSW generation is projected to increase causing more soil, water, and air contamination and is also becoming a public health hazard. Therefore, positive utilization of MSW can mitigate the aforementioned problems and health hazard associated with rise in MSW generation. The production of transportation liquid fuels, from biomass and MSW sources, can be achieved through either thermochemical or biological processes. Examples of these are bio-oil and ethanol from fast pyrolysis and fermentation technology, respectively. Fast pyrolysis, a major thermochemical process, produces bio-oil by decomposition of materials at a higher temperature in the absence of oxygen. Other than bio-oil (the main product) fast pyrolysis also produces biochar and syngas as byproducts. Bio-oil is a promising fuel that can be used in the transportation sector. However, one of the drawbacks

in adopting bio-oil as transportation liquid fuel is its incompatibility with current infrastructures mainly due to undesirable properties. Potential alternative transportation liquid fuels should have comparative properties similar with those of fossil fuels that have high energy-density, chemical stability, and superior combustion characteristics. Bio-oil have undesirable properties of high oxygen and water content, resulting in low energy density. Similarly, acidic property makes it corrosive in nature. There are severed routes employed to tackle these undesirable properties of bio-oil. Routes such as hydrodeoxygenation, which is operated at higher temperature and with hydrogen under high pressure, and convert liquid fuels derived from pyrolysis of biomass chemically similar to those of fossil fuels are receiving great attention. However, the major drawbacks of hydrodeoxygenation are high pressure operation and high quantity of hydrogen required for deoxygenation of bio-oil. Another example is the use of catalysts in fast pyrolysis of biomass, however, these routes failed to completely remove oxygen content from bio-oil. Therefore, a novel concept is the application of natural gas and catalysts in fast pyrolysis to provide hydrogen required for deoxygenation and formation of aromatic hydrocarbons in bio-oil. In chapter II, fixed-bed pyrolysis, and pyroprobe attached with gas chromatography/mass spectrometry (py-GC/MS) were employed to evaluate the effect of catalytic pyrolysis of eastern red cedar with methane over catalysts (HZSM-5 and MoZn/HZSM-5) on bio-oil properties (chemical composition, yield, and energy). In Chapter III, py-GC/MS was used to carry out co-pyrolysis of methane with MSW at a temperature of 550, 650, and 750°C, and catalyst (HZSM-5, HZSM-5 and control).

The overall goal of this study was to scale up develop a novel technology at lab-scale to convert methane and biomass (eastern red cedar) or MSW synergistically into liquid hydrocarbon fuels via fast pyrolysis over HZSM-5 supported catalysts.

The specific objectives were to:

1. Investigate the effect of catalytic fast co-pyrolysis of methane and raw eastern red cedar over HZSM-5 supported catalysts on the chemical composition, yield of aromatics hydrocarbons and weight yield of liquid fuels (bio-oil) using a pyroprobe reactor and a laboratory scale fixed-bed reactor.
2. Investigate the effect of catalytic fast co-pyrolysis of methane and raw municipal solid waste over HZSM-5 catalysts in a pyroprobe reactor on the chemical composition and yield of aromatics hydrocarbons.

CHAPTER II

2 CATALYTIC PYROLYSIS OF RAW EASTERN RED CEDAR IN METHANE ATMOSPHERE TO FORM UPGRADED BIO-OIL

Abstract

Fast pyrolysis is a promising route to transform biomass into renewable bio-oil that can be used in the transportation sector. However, use of bio-oil as a source of transportation fuels suffers from several technical challenges due to its adverse physical and chemical properties, such as high acidity, viscosity, oxygen and water content, and low energy content. This study focused on the investigation of the performance of fast co-pyrolysis of methane and eastern red cedar over molybdenum modified bimetallic (MoZn/ZHSM-5) and HZSM-5 support catalysts on improving properties of bio-oil. The fast co-pyrolysis experiments were conducted at the temperature of 650 and 750℃ in a laboratory scale fixed bed reactor and py-GC/MS. The maximum bio-oil yield, energy density and energy recovery of 53.4%, 10.2MJ/kg, and 29.9%, respectively, were all achieved under methane atmosphere over MoZn/HZSM-5 at 650℃ using fixed bed reactor. Several compounds grouped as acids, alcohols, aldehydes, benzene derivatives, BTEXs, furans, ketones, PAHs, and phenols were detected in bio-oil in which phenols dominated in most conditions. Aromatics hydrocarbon was improved to the maximum yield of about 57.6% (peak area) under methane over MoZn/HZSM-5 at 750℃ in fixed bed reactor. Results from py-GC/MS showed a significant reduction in oxygenated compounds in the MoZn/HZSM-5 under methane at 750℃.

2.1 Introduction

Fast co-pyrolysis of methane and biomass could be a potential effective technology that would produce biofuel liquids with desired quality and high aromatics hydrocarbons. The effectiveness of the novel technology in the production of alternative renewable liquid fuels could be comparable to the currently available hydrodeoxygenation (HDO) and other hydroprocessing techniques which are expensive [1, 2]. The non-renewability and adverse environmental effects of fossil fuels, which continue to dominate the supply of transportation fuels, has encouraged a search for renewable and environmental-friendly alternative sources [3]. Renewable transportation fuels can be produced from biomass through thermochemical, fermentation and other processes. Eastern red cedar, a problematic plant in Oklahoma, can be utilized as one of the feedstock. Report on the utilization of eastern red cedar as feedstock for transportation fuels are limited in the literature [4, 5]. Biomass fast pyrolysis, which produces bio-oil is one of the preferred technologies that have the potential of providing renewable alternative transportation fuels [6]. However, use of bio-oil faces several technical challenges due to its adverse properties. Bio-oil has high water, and oxygen content, high viscosity, acidity, and chemical instability that make it unsuitable for storage and technically challenging for converting into transportation fuels [7, 8, 9]. These undesirable properties are primarily associated with a massive quantity of oxygenated compounds (ketones, phenolic, guaiacols, aldehydes, furan, carboxylic acids and polyols) found in bio-oil [10, 11, 12]. Therefore, elimination of oxygen from bio-oil is critical for upgrading bio-oil to use as transportation fuel using current infrastructures. Hydrodeoxygenation and catalytic cracking techniques using zeolites (X, Y, beta, ZSM-5, etc) and metal base (Si, Al, Pt, Ni, Co, Pd, Ru, etc) catalysts

have been investigated to upgrade fast biomass bio-oil [13, 14, 15]. Most zeolites catalysts without metal have shown fast deactivation, low deoxygenation and hydrogenation effects leading to low selectivity of aromatic hydrocarbons, low removal of oxygenates and high coke deposition.

Metal base catalysts have low acidity resulting in poor isomerization and cracking [15, 16]. However, acid zeolites catalysts, that have a small pore size and both weak and strong acid sites, such as ZSM-5, demonstrated the highest performance in upgrading biomass pyrolysis bio-oil to aromatic hydrocarbons. HZSM-5 allows diffusion of small molecules through its small pores that promote the formation of lighter aromatics compounds. HZSM-5 possesses both weak and strong acid sites of which strong acid is more active in catalyzing waxes and heavier hydrocarbon into lighter aromatic compounds. Due to small pore size, HZSM-5 has a low rate of deactivation, unlike other catalysts with large pore sizes that allow the formation of bulky coke that blocks the pore, leading to faster deactivation of the catalysts [16, 17, 18, 19, 20].

Upgrading of bio-oil by deoxygenation in form of mainly H_2O during fast catalytic pyrolysis of biomass requires feedstock with a high ratio of hydrogen to a carbon atom (H/C) [8]. However lignocellulosic biomass has a lower H/C ratio (0.5) in comparison to petroleum-based feedstock (H/C ratio from 1 to 2) [21]. Low hydrogen and high oxygen contents of biomass convert into bio-oil with high oxygenated compounds resulting in bio-oil's undesirable properties, such as high acidity, poor stability, and low heating value. Thus, the addition of hydrogen and removal of oxygen are essential to upgrade bio-oil with lighter hydrocarbons [22]. Bio-oil oxygen is removed during fast pyrolysis of biomass in the form of CO, CO_2, and H_2O. Additional hydrogen during fast pyrolysis of biomass

favors removal of oxygen in form of H_2O than as CO and CO_2. Thus, the addition of hydrogen during fast pyrolysis or bio-oil upgrading improves bio-oil properties by reducing oxygenates and increasing carbon yield by retaining carbon [21, 22].

Incorporating methane into bio-oil can provide additional hydrogen required for upgrading of bio-oil with low oxygenates and high lighter hydrocarbons making bio-oil more compatible with petroleum intermediates. The additional hydrogen is produced from thermal decomposition, and catalytic reforming of methane with carbon dioxide [23, 24, 25]. However, decomposition of methane occurs at a temperature higher than 900°C, hence, catalysts and appropriate reaction conditions are needed to reduce decomposition temperature to about 650°C, close to fast pyrolysis temperature [26]. Fast pyrolysis of biomass produces high CO_2 that can also be used for dry reforming of methane to produce synthesis gas (H_2 and CO) [27]. Additional of hydrogen and carbon from thermal and catalytic cracking of methane increases atomic H/C ratio during biomass fast pyrolysis [28]. Therefore, high H/C can promote the formation of saturated and favorable aromatics hydrocarbons to improve bio-oil.

The performance of catalyst and pyrolysis temperature are particularly important in activation of methane in fast pyrolysis. A study on the performance of ZSM-5 catalyst loaded with several metals (Fe, Co, Cu, Mn, Zr, Ni, Ce, and Zn) on co-pyrolysis of biomass and methane was investigated in-situ [1]. The authors found that Zn/ZSM-5 improved aromatics but lower bio-oil yield. The improvement of aromatic hydrocarbons was also reported in a previous study [2] where MoZn/HZSM-5 catalysts were used in co-catalysis of methane and, torrefied and raw switchgrass in the pyroprobe reactor, but the study did not report on the yield of bio-oil. Thus, the purpose of this research was to investigate co-

pyrolysis of methane and raw eastern red cedar using a fixed-bed reactor and a pyroprobe reactor over HZSM-5 and MoZn/HZSM-5 catalysts for improvement of aromatic hydrocarbons and yield of bio-oil. The bio-oil yields, aromatic hydrocarbons yield, and aromatics selectivity of benzene, toluene, ethylbenzene, and xylene (BTEX), and polyaromatic hydrocarbons (PAHs) were analyzed. The results of the chemical composition of bio-oil from fixed bed were compared with those from a pyroprobe reactor to demonstrate how different reactor types affect chemical properties.

2.2 Materials and Methods

2.2.1 Feedstock

Raw eastern red cedar was shredded and supplied by Custom Wood Fibers & Cedar Mulch LLC (Stillwater, OK, USA). The eastern red cedar was ground using Thomas Model 4 Wiley® Mill (Thomas Scientific, Swedesboro, NJ, USA) fitted with a 150µm screen. Therefore, the particular size of biomass sample was about 150µm. The ground eastern red cedar was placed in zip-locked plastic bags and kept in storage at room temperature. The ultimate and proximate (Table 1) analyses of the eastern red cedar were performed by Hazen Research, Inc. (Golden, CO, USA).

Table 1. Ultimate and proximate analysis of Eastern Red-cedar

	Parameters	Eastern red cedar
Ultimate Analysis (dry wt.%)	Carbon	55.14
	Hydrogen	5.88
	Nitrogen	0.20
	Sulfur	0.01
	Oxygen	38.77
Proximate Analysis (wet wt.%)	Moisture	10.39
	Ash	1.14
	Volatile	70.17
	Fixed carbon	18.3
Energy content (MJ/kg)	High Heating Value	17.68
	Low Heating Value	16.31

2.2.2 Catalyst characteristics

Powder and pellet HZSM-5 and molybdenum bimetallic (MoZn/HZSM-5) catalysts were used for catalytic pyrolysis in this study. Powder ZSM-5, in the form of ammonium, was purchased from Zeolyst International, (Conshohocken, PA, USA), whereas pellet ZSM-5 was purchased from ACS Material LLC (Medford, MA, USA). The pellet ZSM-5 zeolite has a $SiO_2/Al2O_3$ molar ratio of 38 and specific surface area of 250 m^2/g, while the powder ZSM-5 has a $SiO_2/Al2O_3$ molar ratio of 30 and specific surface area of 400 m^2/g. The pellet ZSM-5 had a diameter of 2 mm and length of between 2 to 10 mm. ZSM-5 catalyst was calcined in a furnace at 500°C for 6h under air atmosphere to form protonated HZSM-5. A detailed description of the route for the synthesis of MoZn/HZSM-5 is reported elsewhere [29]. HZSM-5 and MoZn/HZSM-5 were loaded in a container and kept in storage at room temperature before using in tests. Catalysts in

powder and pellet forms were used in pyroprobe and fixed reactor reactors, respectively. Powder catalyst could not be used in the fixed bed reactor because it could not be contained in the reactor as the carrier gas carried it away. While pellets catalyst could not be used in the pyroprobe reactor because of the limitation of size.

2.2.3 Experimental design

The experimental design used in this study was a full factorial with three parameters (temperature, catalyst, and atmosphere) of 2 × 3 × 2 levels. Pyrolysis temperature had two levels of 650 and 750℃, catalyst had three levels of HZSM-5, MoZn/HZSM-5, and Control), and atmosphere had two levels of methane and nitrogen (for experiments using a fixed reactor) or helium (for using a py-GC/MS). All experiments were carried out at least in triplicate. Statistical Analysis System (SAS® version 9.4) was engaged to perform statistical analysis in order to evaluate the effects of factors and their interaction on bio-oil properties studied. Pro GLM was used to perform a three-way analysis of variance (ANOVA) for testing the main effects (temperature, catalyst and atmosphere) and their interaction. A significant difference between the means was concluded to exist if the p value is less than 0.05.

2.2.4 Fixed bed fast co-pyrolysis

The fixed-bed reactor (shown in Figure 1) was modified to suit pyrolysis experiments from a fixed-bed reactor that was used biomass gasification by Sarkar et al. (2014) [30]. The apparatus consists of a fixed stainless steel tube reactor with about 2.54cm diameter and 90cm length, hooper, biochar collector (bottom) a fixed bed, and a condenser. Complete detail of the fixed-bed reactor setting up is described elsewhere [30], whereas modifications done are described in this paper. The fixed reactor was modified at gas

(methane and nitrogen) inlet and pyrolysis vapor outlet. Gas inlet was placed at the top to allow preheating of gas to a temperature, at which pyrolysis experiment was carried out, while flowing toward fixed-bed. The outlet was connected to a condensation system through a transfer line that was kept heated during fast pyrolysis. The transfer line was maintained at 300°C to minimize the effect of secondary reactions and to avoid condensation of pyrolysis vapor before reaching the condensers. High temperatures with longer residence time increase secondary reactions. Some heavier compounds condense at a temperature lower than 300°C. Condensation system was made of 4 condensers submerged in the coolant that was kept at a temperature less than -10°C.

The reactor was heated using vertical split-hinge tube furnace (model TVS 12/600, Carbolite Inc., WI, USA). Prior to starting the experiment, the reactor was purged with high purity nitrogen (99.99%) at a flow rate of 1.5 l/min for 10 minutes to eliminate the presence of oxygen and moisture in the reactor. About 10 g of catalyst (HZSM-5 or MoZn/HZSM-5) pellets was loaded on the reactor bed made of metal mesh. To keep the ratio of catalyst and biomass at 1:1, eastern red cedar sample of about 10g was loaded in the feeding hooper. Under nitrogen atmosphere, the flow rate of nitrogen was maintained at about 3 l/min. While, under the methane atmosphere, methane (99.99% purity) was fed into the reactor at a flow rate of about 3 l/min. To start the fast pyrolysis experiment, biomass sample was dropped into the reactor by slowly opening the ball valve to allow smooth flow. Bio-oil was obtained in the condenser by quenching pyrolysis vapors at about -10°C. Bio-oil samples were placed in a 20 ml plastic bottle and stored at 4°C temperature in the fridge for further analysis. Biochar samples were collected from the bed and biochar

collector at the reactor bottom. Biochar, in a ceramic crucible, was placed in a vacuum desiccator for about 24h before weighing.

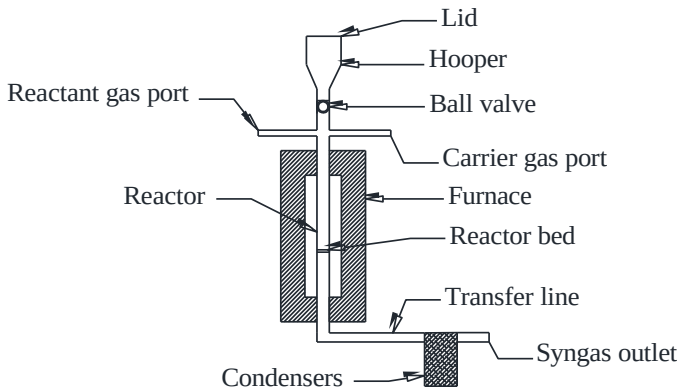


Figure 1. Schematic of the fixed-bed reactor. Sarkar et al. (2014) fixed-bed gasifier modified for pyrolysis experiments.

2.2.5 Fast pyrolysis in pyroprobe

The fast pyrolysis experiments in the pyroprobe reactor were performed using Pyroprobe (Model 5200, CDS Analytical Inc., Oxford, PA, USA) connected to Gas Chromatograph/Mass Spectrometry (GC/MS, Model 7890A/5975 C, Agilent Technology). The pyroprobe consisted of a filament rod, an adsorbent trap (Tenax-TA^{TM}) and reactant gas operation option. The GC/MS used was fitted with a DB-5 capillary column with dimensions of 30 mL×0.32 mm internal diameter and 0.25 µm film thickness. Sample preparation and experimental procedure are described in detail in the previous study [31]. Methane (99.99% purity) was used as a reactant gas for fast pyrolysis under methane atmosphere. Unlike fixed-bed pyrolysis where nitrogen was used as atmosphere, in pyrolysis GC/MS, helium was introduced in place of nitrogen. The pyrolysis experiments

were performed by loading about 0.3 mg of biomass sample and 3.0 mg of catalyst (powder) into a quartz tube. Unlike in fixed bed experiment, the ratio of biomass to catalyst in py-GC/MS experiment was 1:10, which was similar to the ratio used in previous study [2] . Similar ratio allowed us to compare the effect of different biomass used. Quartz wool was used to hold and separate biomass sample and catalyst in tube quartz, where biomass was inserted between the two half loads of catalyst. The experiment was then started remotely from a computer. The procedure of performing the fast pyrolysis experiments in py-GC/MS is reported in previous studies [2, 32]. Pyrolysis products desorbed at 300°C from the adsorbent trap and was introduced into an online GC/MS for analysis of chemical compositions using Agilent chemstation software to quantify and integrate peaks. The peaks were compared with the National Institute of Standard Technology (NIST) mass spectral library data.

2.2.6 Products analysis

2.2.6.1 Products yields

The products (bio-oil, biochar, and syngas) derived from fast pyrolysis of eastern red cedar using fixed-bed were collected to analyze their properties. Bio-oil was collected from condensers while biochar was collected from bed reactor and biochar collector. The weight of bio-oil and biochar were measured, whereas, syngas yield was determined by weight difference. Thus, the yield of bio-oil, biochar, and syngas (%w/w) were calculated by dividing the weight of each with the weight of biomass used times 100%. However, for fast pyrolysis experiment in pyroprobe, the product yields could not be determined but the composition of bio-oil was identified by the GC/MS.

2.2.6.2 Bio-oil analysis

The composition of bio-oil obtained from the fixed-bed reactor was identified offline using the GC/MS. The bio-oil sample was prepared by diluting bio-oil with acetone in a 1:10 ratio (w/w). Bio-oil was homogenized by thoroughly stirring before mixing the sample with acetone. About 1 microliter of the prepared bio-oil sample was injected in the GC/MS using a 10 microliter syringe. The details of analysis procedure used are described in a previous study [31].

The energy content (gross heating value, MJ/kg) of bio-oil was determined using a bomb calorimeter (6100 Calorimeter, Parr Instruments, IL, USA) following a standard test technique for determination of energy content of biofuel liquids (ASTM D4809). About 0.5 g of bio-oil was loaded in a nickel crucible and placed in the bomb calorimeter. The bomb calorimeter was filled with oxygen, and dropped into calorimeter jacket containing about 2000 ml of deionized water. The energy content was determined without accounting for water content which was unknown.

2.2.6.3 Py-GC/MS – Chemical composition analysis

The chemical composition of pyrolysis products obtained from experiments using a pyroprobe reactor were analyzed online with GC/MS. The procedure of the chemical composition analysis was similar to that used to analyze the composition of the bio-oil obtained from the experiments using a fixed-bed reactor, as described earlier.

2.3 Results and discussion

2.3.1 Feedstock characteristics

Ultimate and proximate analyses of eastern red cedar used are presented in Table 1. Properties of bio-oil heavily depend on feedstock. The high content of oxygen leads to

more formation of oxygenated compounds that with water content reduce the energy density of bio-oil. Ash content is considered to have a catalytic effect on pyrolysis and gasification of biomass. However, due to the low ash content of 1.1 %wt on a wet basis (w.b.), these effects were not taken into consideration [33]. Like other lignocellulosic biomass, the eastern red cedar had a high oxygen and moisture content of 38.8 %wt and 10.4 %wt (w.b.), respectively. High oxygen and moisture content driven several authors to study effects of lowering oxygen and moisture content through torrefaction on the bio-oil properties [2, 34]. Most of these studies reported that torrefaction lowered moisture and densified energy contents of biomass, however torrefaction requires additional unit operations that lower energy efficiency to utilize biomass as feedstock for production of fuels.

2.3.2 Fixed bed fast co-pyrolysis

Analysis of bio-oil derived obtained using the fixed-bed reactor are discussed below.

2.3.2.1 Products distribution

The pyrolysis products (bio-oil, biochar, and syngas) distribution on a weight basis are presented in Figure 2 (a & b). The lowest yield of bio-oil of 38.7%wt was recorded when HZSM-5 support was used under methane atmosphere at a high temperature of 750°C. Whereas the highest yield of bio-oil of 53.4%wt was obtained when MoZn/HZSM-5 was used under methane at 650°C. These results were in agreement with results of a previous study that found MoZn/HZSM-5 to be more effective in activation of methane compared to other molybdenum modified catalysts (MoO_3/HZSM-5, Mo_2C/HZSM-5) [2]. The results demonstrated that applying methane over the catalyst in fast pyrolysis of

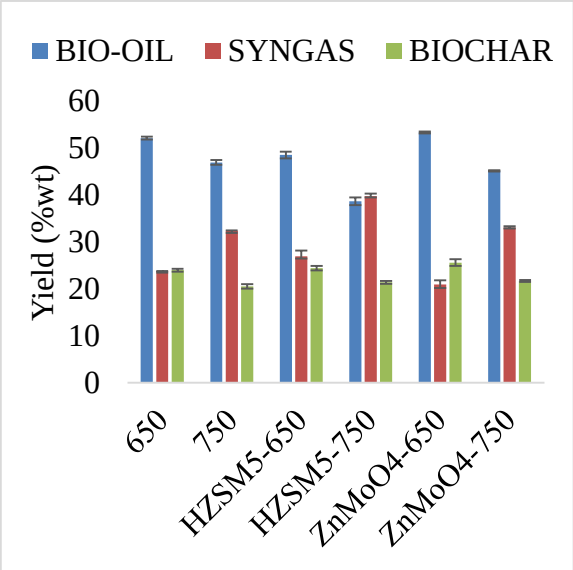
biomass has significant effects on yields of pyrolysis products. As shown in Table 2, pyrolysis temperature (650 and 750°C), atmosphere (methane and nitrogen) and catalyst (MoZn/HZSM-5, HZSM-5 and control) and their interactions had significant effects on the yield of bio-oil and syngas. Temperature of 650°C demonstrated higher performance toward high yield of bio-oil when compared with temperature of 750°C, over all the pyrolysis conditions. Higher temperatures lowered the yield of bio-oil from an average of 49.7 to 43%wt at a temperature of 650 and 750°C, respectively. In nitrogen, non-catalytic fast pyrolysis seems to show a higher yield of bio-oil at both temperatures as compared to catalytic fast pyrolysis. The effects of interactions that were significant on both bio-oil and syngas yields were further investigated by observing the yield mean values as presented in Table 3 and 4. The mean yields of bio-oil as affected by the interaction of temperature and catalyst, was in the order of control > HZSM-5 > MoZn/HZSM-5 at 650°C, but at 750°C yields was in the order of control > MoZn/HZSM-5 > HZSM-5. Methane performed better over MoZn/HZSM-5 and control on the improvement of bio-oil yield, but less effective over HZSM-5 when compared to nitrogen. The effects of MoZn/HZSM-5 under nitrogen at 650 and 750°C was negative while under methane at 650°C was positive. HZMS-5 had only positive effects on the bio-oil yield when interacted with nitrogen at 650°C, while with other levels of the atmosphere and temperature were negative.

Distributions of syngas were in the range of 21 to 39.8%wt under methane and 24 to 38.6%wt under nitrogen. Syngas yield obtained under methane over HZSM-5 catalyst at a temperature of 750°C was the highest at 39.83%wt. Lowest syngas yield was found under methane over MoZn/HZSM-5 catalyst at 650°C. Syngas yield increased under all combination of main factors when temperature increased from 605 to 750°C. High

temperature increases secondary reactions and tar tracking that favor formation of non-condensable pyrolysis gases, hence, increases syngas yield [35].

Biochar yield was significantly influenced by temperature, while atmosphere and catalyst had no significant effect. As temperature increased from 650 to 750°C, the yield of biochar decreased from an average of 24 to 25%wt. While the reduction in biochar yield due to increase in temperature did not result in increased bio-oil yield, syngas yield did increase. Contribution to the increased syngas yield as temperature increased is mostly due to cracking of tars/volatiles [36]. The main focus of fast pyrolysis of biomass is bio-oil, biochar is an unwanted by-product [12, 37]. However, biochar has a potential to be used in soil improvement, storage of carbon, mitigation of climate change, water purification and others [37, 38, 39].

(a) Under methane atmosphere



(b) Under nitrogen atmosphere

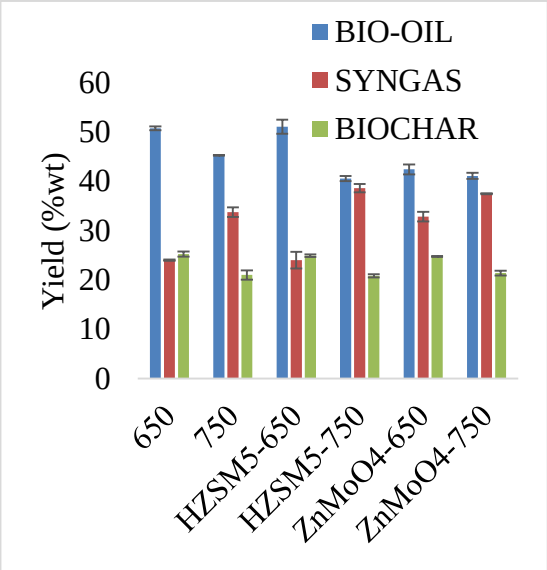


Figure 2. Bio-oil, biochar, and syngas yields (%wt) from pyrolysis of eastern red cedar under methane and nitrogen in catalytic (HZSM-5 and MoZn/HZSM-5) and non-catalytic pyrolysis at 650 and 750°C.

Table 2. P-values from statistical analysis of means: Effects of pyrolysis temperature (Temp), catalyst (Cat), and atmosphere (Atm) on yields of pyrolysis products (bio-oil, syngas, and biochar)

Product yields	Temp	Atm	Cat	Temp * Atm	Temp * Cat	Cat * Atm	Temp * Cat * Atm
Bio-oil	<.0001	0.0001	<.0001	0.0324	0.0004	<.0001	0.0043
Syngas	<.0001	0.0008	0.0002	0.1461	0.0022	<.0001	0.0049
Biochar	<.0001	0.8563	0.2006	0.4744	0.9178	0.1743	0.5037

Temp, Atm, and Cat mean independent variable temperature, atmosphere, and catalyst, respectively.

Table 3. Effects of interaction of three factors (catalyst vs. atmosphere vs. temperature) on yield of bio-oil and syngas.

Products (mean %wt)	Treatment conditions	Nitrogen 650°C	750°C	Methane 650°C	750°C
Bio-oil	Control	50.7±0.5	45.2±0.1	52.2±0.4	47.0±0.7
	HZSM-5	51.1±2.0	40.5±0.7	48.6±1.0	38.7±1.1
	MoZn/HZSM-5	42.4±1.4	41.1±0.8	53.4±0.3	45.2±0.2
Syngas	Control	24.0±0.2	33.7±1.4	23.8±0.1	32.4±0.1
	HZSM-5	24.0±2.4	38.6±1.2	27.0±1.7	39.8±0.7
	MoZn/HZSM-5	32.8±1.3	37.5±0.1	21.0±1.3	33.1±0.4

Table 4. Effects of interactions of two factors (catalyst vs. temperature, and catalyst vs. atmosphere) on the bio-oil and syngas yields.

Products (mean %wt)	Catalyst	Temperature (°C)		Atmosphere	
		650	750	Nitrogen	Methane
Bio-oil	Control	51.5±0.9	46.1±1.1	48.0±3.2	49.6±3.0
	HZSM-5	49.8±1.9	39.6±1.3	45.8±6.2	43.6±5.7
	MoZn/HZSM-5	47.9±6.4	43.1±2.4	41.7±1.2	49.3±4.8
Syngas	Control	23.9±0.1	33.1±1.1	28.9±5.7	28.1±5.0
	HZSM-5	25.5±2.4	39.2±1.1	31.3±8.6	33.4±7.5
	MoZn/HZSM-5	26.9±6.9	35.3±2.6	35.2±2.8	27.0±7.1

2.3.2.2 Energy content and yield of bio-oil

The energy content and yield of bio-oil recovered under all the pyrolysis conditions are shown in Figure 3 and Figure 4 as yield (% MJ/MJ) and density (MJ/kg), respectively. Bio-oil have a lower energy content between 15 – 20 MJ/kg as compared to crude oils with 40 – 42 MJ/kg [7], therefore bio-oil requires upgrading to be compatible. Incorporation of methane has increased the energy density of bio-oil (from 4.2 – 8.5 MJ/kg under nitrogen to 4.65 – 10.2 MJ/kg under methane). Catalytic conditions reduced the energy density of bio-oil obtained under both methane and nitrogen atmosphere. Although the highest yield of bio-oil was achieved over MoZn/HZSM-5 catalytic pyrolysis, bio-oil may contain more water or oxygenates that reduced its energy density. A previous study [40] on pyrolysis of woody biomass reported that high water content of 13.9, 16.7, 13.0, and 14.4 wt% when HBeta-25, HY-12, HZSM5-23 and HMOR-20 catalysts were used, respectively. While lowest water content of 5.4 wt% was obtained when no catalyst was used. With increase in temperature from 650 to 750℃, the energy density of bio-oil decreased. The energy contents of bio-oil were determined without removing water content, which reported in literature as a dominant compound in typical biomass delivered bio-oil with a load of 15 – 30%wt water content [41, 42, 8]. The reported energy contents of the all bio-oil were not corrected to account for water content, thus the energy contents (3.8 – 10.2 MJ/kg) were lower compared to 15 – 20 MJ/kg of typical bio-oil reported in the literature [7, 41, 43].

Percentage of energy retained in bio-oil from pyrolysis of eastern red cedar under all conditions was analyzed. The highest energy yield (29.98%) was achieved in non-catalytic pyrolysis at 650℃ under methane atmosphere. The lowest energy yield (8.9 %) was found in catalytic (MoZn/HZSM-5) pyrolysis at 750℃ under nitrogen atmosphere.

The presence of catalysts and high temperatures reduced energy yield in both methane and nitrogen atmosphere, possibly because of formation of more water as a result of deoxygenation reactions promoted by the catalyst.

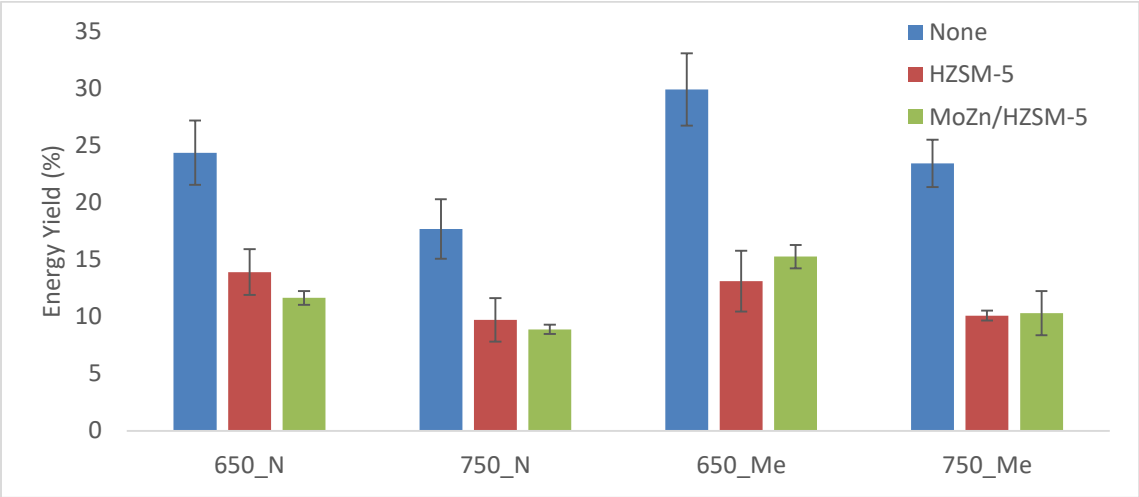


Figure 3. Energy yield (%) of the bio-oil from fast pyrolysis of eastern red cedar under methane (Me) and nitrogen (N) in catalytic (HZSM-5 and MoZn/HZSM-5) and non-catalytic pyrolysis at 650 and 750°C.

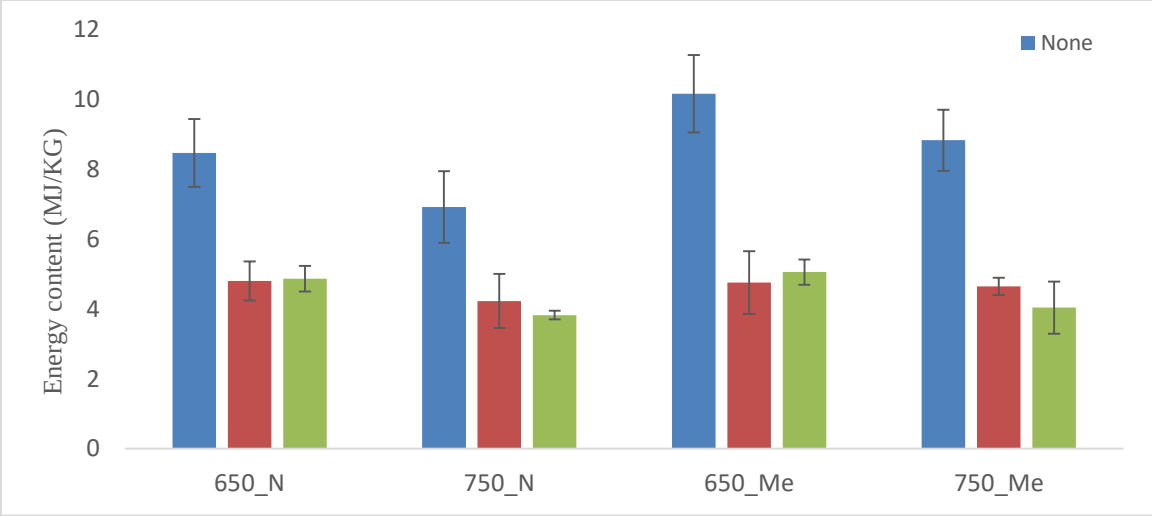


Figure 4. Energy content (MJ/kg) of bio-oil obtained under methane (Me) and nitrogen (N) in catalytic (HZSM-5 and MoZn/HZSM-5) and non-catalytic fast pyrolysis at 650 and 750°C.

2.3.2.3 Fixed bed – Chemical composition of bio-oil

Composition of bio-oil, a complex mixture of organic compounds, is dependent on pyrolysis conditions and feedstock properties. Hundreds of chemical compounds have been identified in bio-oil and tabulated in several reports [35, 40, 41, 43, 44]. Thus, analysis and reporting of chemical characteristics of bio-oil vary. In this study, chemical compositions of the bio-oil were identified using GC/MS and classified based on functional groups of acids, alcohols, aldehydes, benzene derivatives, BTEX (benzene, toluene, ethylbenzene, xylene), furans, ketones, olefins, PAHs (polyaromatic hydrocarbons), and phenols as shown in Table 5 (a & b). These groups were quantified as peak area (%), which is a relative amount of each group as compared to the amount of total compounds identified in the bio-oil sample. Phenolic compounds are dominant in all bio-oil regardless of the pyrolysis conditions. Phenols with ketones and aldehydes are the most abundant group of compounds found in the bio-oil from non-catalytic pyrolysis at both pyrolysis temperatures. As temperature increased, phenols yield slightly increased in both catalytic and non-catalytic pyrolysis conditions under nitrogen. This result is consistent with a previous study that has shown an increase in phenolic species, such as phenol, 2-methyl-phenol, 3-methyl-phenol, and 1,2-benzenediol) with increase in pyrolysis temperature [45]. The introduction of methane over MoZn/HZSM-5 reduced phenolic species. For example, phenolic accounted for 44% of total peak areas in non-catalytic at 750°C and reduced to 25% peak area when methane and MoZn/HZSM-5 were introduced at 750°C. Under methane at 750°C (Table 5 (b)), MoZn/HZSM-5 was effective in reducing oxygenated groups, such as acids, alcohols, ketone, and aldehydes when compared under nitrogen at the same temperature. Reduction in compounds such as phenolic, ketones and aldehydes may minimize problems associated

with using bio-oil containing those compounds. For example, using bio-oil that is high in phenols causes damage to thin metallic materials used in machines such as seals and gaskets [22]. When HZSM-5 and ZnMoO4/HZSM-5 were used under both atmosphere, the aldehyde compounds were not detected in bio-oil. Methane over MoZn/HZSM-5 at a high temperature of 750°C increased aromatics hydrocarbons as compared to nitrogen. At this condition (using Methane and MoZn/HZSM-5 at 750°C), benzene derivatives, BTEXs and PAHs increased from about 2.4%, 3.9%, 1.7% in non-catalytic under nitrogen to 15.9%, 16.5%, 24.3%, respectively.

Table 5. Chemical composition (peak area %) of bio-oil from pyrolysis of eastern red cedar using a fixed bed reactor.

	Under Nitrogen Atmosphereosphere					
Group	650	750	HZSM5-650	HZSM5-750	MoZn/HZSM-54-650	MoZn/HZSM-5-750
Acids	2.7±0.0	6.5±3.7	0.9±0.6			1.7±0.2
Alcohols	4.6±2.3	5.7±0.1		1.0±0.2	13.5±0.4	
Aldehydes	25.8±3.2	16.8±3.5	1.3±0.4	0.5±0.1	0.9±0.1	0.9±0.1
Benzene Derivatives	2.4±1.1	3.4±0.4	3.7±0.3	12.6±0.2	15.2±1.1	8.8±1.1
BTEX	3.9±0.1		9.1±0.6	12.0±0.6	2.8±0.9	6.4±0.6
Furans	2.5±1.6	3.4±1.2	5.0±1.6	2.5±1.4	10.2±1.7	13.7±0.7
Ketones	14.0±2.1	4.3±1.5	11.3±3.9	10.3±1.7	1.7±0.1	5.8±0.6
Olefins			2.4±1.5	1.0±0.8		
PAHs	1.7±0.3	1.6±0.3	3.4±0.7	7.5±0.2	18.8±0.4	11.4±1.2
Phenols	34.6±4.8	38.6±4.3	41.9±3.0	45.2±0.5	32.7±3.7	42.1±2.0

(a) Nitrogen used as atmosphere

	Under Methane Atmosphere					
Group	650	750	HZSM5-650	HZSM5-750	MoZn/HZSM5-650	MoZn/HZSM5-750
Acids	1.0±0.2	1.5±0.2	1.2±0.1	1.0±0.1	2.8±1.1	
Alcohols	3.6±1.9	15.9±3.0	8.9±3.2	4.3±0.7	16.2±0.2	1.9±0.9
Aldehydes	17.3±0.2	17.0±3.1	3.6±0.7	0.3±0.1	1.8±0.7	
Benzene Derivatives	1.1±0.2	1.7±0.4	11.4±3.5	11.7±0.8	4.9±1.1	15.9±1.6
BTEXs	1.1±0.5	1.7±0.1	11.4±1.3	19.6±0.3	6.1±0.3	16.5±1.0
Furans	1.4±0.5	1.6±0.2	0.2±0.2	1.3±0.2		2.4±0.7
Ketones	15.3±1.1	6.1±1.7	11.7±2.9	6.4±0.2	7.4±1.9	3.0±0.7
Olefins	0.4±0.1	0.9±0.3				6.8±0.1
PAHs	1.7±0.4	1.3±0.4	11.8±0.3	15.9±0.7	3.9±0.3	24.3±1.3
Phenols	48.6±2.1	44.2±3.2	31.8±1.8	38.5±2.3	47.3±3.4	25.2±1.8

(b) Methane used as atmosphere

The total yields of aromatics hydrocarbons (PAHs, BTEX and benzene derivatives) obtained using the fixed-bed reactor are presented in Table 6. The yields of aromatics hydrocarbons obtained from non-catalytic fast pyrolysis under both atmospheres at temperature of 650 and 750°C were between 4.2 to 7.9%. The yields increased significantly in the presence of both catalysts under all other pyrolysis conditions. For example, total aromatics hydrocarbons yield increased from 5.2% in non-catalytic condition to a maximum yield of 56.8% under methane over MoZn/HZSM-5 at temperature of 750°C. Comparing catalysts, highest aromatic hydrocarbons yields achieved over HZSM-5 and MoZn/HZSM-5 were 47.14% and 56.8% respectively, all under methane. The highest aromatics hydrocarbons yield under nitrogen was 36.9%, which was lower than yields under methane over both catalysts at 750°C, indicating that introduction of methane as a hydrogen donor in fast pyrolysis at high temperature improved aromatic hydrocarbons yield. The yields with the introduction of methane over HZSM-5 catalysts are similar to the yield (53.7%) reported a previous study [46] where methanol was used as a hydrogen

donor. When HZSM-5 and MoZn/HZSM-5 compared under nitrogen only, modified catalyst (MoZn/HZSM-5) was more effective in the production of aromatics hydrocarbons at 650 than at 750℃. A similar trend of results was reported in a previous study [47] in which modified Ga/ZSM-5 catalyst achieved high carbon yields of 23.2 and 17.5% as compared to yields of 15.4 and 11.5% over ZSM-5 at 550 and 600℃, respectively.

Table 6. Total aromatics yield (area %) from non-catalytic and catalytic under different pyrolysis conditions

Pyrolysis Atmosphere	Under nitrogen atmosphere		Under methane atmosphere	
Pyrolysis Temperature (℃)	650	750	650	750
Non- catalytic	7.93±1.82	5.06±0.76	4.22±1.06	5.19±1.26
HZSM-5	24.14±3.07	32.03±2.73	35.52±5.65	47.14±2.82
MoZn/HZSM-5	36.88±2.51	26.63±3.08	14.96±2.16	56.79±4.98

2.3.2.4 Fixed bed - Aromatics selectivity

Table 7 illustrates how selectivity of aromatic compounds (benzene, toluene, ethylbenzene, xylene, benzene derivatives and PAHs) vary with temperature, catalyst, and introduction of methane. Aromatics selectivity (%), was defined as the percentage of the total peak area of all aromatic compounds (benzene, toluene, ethylbenzene, xylene, benzene derivatives and PAHs) that was taken by a specific group of aromatic compound. Benzene and ethylbenzene had the least selectivity among aromatics hydrocarbons. For example, no benzene and ethylbenzene were detected in the bio-oil obtained from non-catalytic. However, the highest benzene selectivity of 2.2% was obtained under nitrogen over HZSM-5 at 650℃, while for ethylbenzene was 1.3% under methane over MoZn/HZSM-5 at 750℃. Benzene selectivity was only significantly influenced by the interaction of atmosphere and catalyst, as there was no significant difference among

independent main effects. Whereas, ethylbenzene selectivity was only significantly influenced by the interaction of temperatures and atmosphere. Highest selectivity (15.9% and 15.9%) for benzene derivatives and PAHs were achieved under methane over MoZn/HZSM-5. Selectivity of benzene derivatives and PAHs increase from their lowest of 1.12% and 1.62% (in non-catalytic) to the highest of 15.9% and 24.4%, respectively when MoZn/HZSM-5 used under methane. Selectivity of xylene in the presence of HZSM-5 was higher than that in the presence of MoZn/HZSM-5. Toluene selectivity increased as temperature increased from 650 to 750°C in catalytic under both methane and nitrogen.

Table 7. Aromatics selectivity (peak area%) of bio-oil obtained fast pyrolysis of eastern red cedar using fixed bed reactor.

Treatment	Aromatics selectivity (peak area %)					
	Benzene	Toluene	Ethylbenzene	Xylene	Benzene derivatives	PAHs
650_Ni		2.6±0.3		1.3±0.2	2.4±1.1	1.7±0.3
750_Ni					3.4±0.4	1.6±0.3
650_Me		0.7±0.2		0.4±0.3	1.1±0.2	1.7±0.4
750_Me		1.2±0.2		0.5±0.3	1.7±0.4	1.2±0.4

(a) Non catalytic fast pyrolysis

Treatment Catalytic (HZSM-5)	Aromatics selectivity (peak area %)					
	Benzene	Toluene	Ethylbenzene	Xylene	Benzene derivatives	PAHs
650_Ni	2.2±0.7	4.8±0.6	0.93±0.1	9.1±1.6	3.7±0.3	3.4±0.9
750_Ni	2.1±0.9	5.2±0.5	0.8±0.1	3.9±0.8	12.6±0.2	7.5±0.2
650_Me	0.4±0.2	3.2±0.1	0.7±0.1	7.8±1.5	11.4±3.5	11.8±0.3
750_Me	0.8±0.1	8.2±0.1	1.2±0.1	9.3±1.0	11.7±0.8	15.8±0.7

(b) Catalytic fast pyrolysis using HZSM-5

Treatment Catalytic (MoZn/HZSM-5)	Aromatics selectivity (peak area %)					
	Benzene	Toluene	Ethylbenzene	Xylene	Benzene derivatives	PAHs
650_Ni	0.3±0.1	0.9±0.2	0.4±0.2	1.1±0.5	15.2±1.1	18.8±0.4
750_Ni	0.5±0.2	1.8±0.4	0.7±0.2	3.5±0.4	8.8±1.1	11.4±1.2
650_Me	0.8±0.2	3.7±0.3	0.6±0.2	1.0±0.2	4.9±1.1	3.9±0.3
750_Me	1.6±0.2	7.4±0.6	1.3±0.2	6.1±1.1	15.9±1.6	24.4±1.3

(c) Catalytic fast pyrolysis using MoZn/HZSM-5

Table 8. P-values from statistical analysis (proc glm) of means: Effects of pyrolysis temperature (Temp), catalyst (Cat), and atmosphere (Atm) on aromatics selectivity

Aromatics	Temp	Atm	Cat	Temp* Atm	Temp* Cat	Atm* Cat	Temp*Atm *Cat
Benzene derivatives	0.489	0.356	0.011	0.989	0.151	0.405	0.008
Benzene	0.373	0.349	0.069	0.387	0.502	0.008	0.813
Toluene	<.0001	<.0001	<.0001	<.0001	0.001	<.0001	0.039
Ethylbenzene	0.062	0.239	0.772	0.002	0.951	0.759	0.271
Xylene	0.019	0.011	0.003	0.331	0.226	0.098	0.708
PAHs	<.0001	<.0001	<.0001	<.0001	0.056	<.0001	<.0001

Means of aromatics hydrocarbons were considered significantly different at p-value of less than 5%
Temp, Atm, and Cat stand for temperature, atmosphere and catalyst

2.3.3 Pyrolysis-GC/MS

The following discusses the results of the chemical composition of pyrolysis products detected and identified by online GC/MS during fast co-pyrolysis of methane and MSW using pyroprobe reactor.

2.3.3.1 Py-GC/MS - Chemicals composition of pyroprobe products

The GC/MS analysis of chemical composition of bio-oil obtained from pyrolysis of eastern red cedar using a pyroprobe (py-GC/MS) are presented in Table 9. Some comparison between data of chemical composition of bio-oil from experiment using a fixed bed reactor

(Table 5) and a pyroprobe reactor linked to GC/MS (Table 9) were observed. The data between those of fixed bed and py-GC/MS were quite different; however, some similarities were observed. For example, similarities were found in non-catalytic pyrolysis under nitrogen atmosphere where aldehydes, ketones, and phenols were the most dominant among the groups. In catalytic, total yield of aromatics hydrocarbons (benzene derivative, BTEX, and PAHs) accounted for nearly 95% (peak area) of bio-oil under all conditions (temperature, atmosphere, and catalyst) in py-GC/MS experiment, while in fixed bed experiment, accounted for about 50% using fixed-bed reactor. This high yield of aromatics hydrocarbons achieved in py-GC/MS experiment can be attributed to the high amount of catalyst used per experiment (biomass to catalyst was 1:10) and use of pyroprobe reactor. A study that investigated the effects of the quantity of ZSM-5 catalyst on aromatic hydrocarbons found that increase in the amount of catalyst resulted in an increase of aromatic hydrocarbons [48]. Phenols were abundant in bio-oil obtained in non-catalytic at 650 and 750°C under both methane and helium using a py-GC/MS, however, HZSM-5 catalyst considerably reduced. The yield BTEX (Table 9) of 6.8 – 10.0% in non-catalytic under increased to about 51.2 – 59.9% when HZSM-5 catalyst was introduced under both methane and helium at 650 and 750°C. These results demonstrated that pore size and acidic properties of HZSM-5 favor formation of lighter compounds, as such similar effects have been reported elsewhere [17].

Table 9. Chemical composition (peak area %) of pyrolysis products from eastern red cedar Py-GC/MS experiments.

	Nitrogen Atmosphere				Methane Atmosphere			
Group	650	750	HZSM5-650	HZSM5-750	650	750	HZSM5-650	HZSM5-750
Acids	0.9±0.5	1.5±1.2	1.5±1.4	***	2.8±1.4	3.5±1.0	***	***
Alcohols	***	1.3±0.2	***	***	1.2±0.4	2.3±0.9	***	***
Aldehydes	12.6±3.3	12.9±2.3	***	***	10.8±1.8	7.1±0.6	***	***
Benzene derivatives	4.1±0.9	4.0±0.2	10.6±0.6	12.9±0.7	5.5±0.3	1.6±0.3	12.3±0.4	12.2±1.5
BTEXs	7.7±2.4	6.8±0.3	53.4±2.2	51.2±2.	10.0±0.6	8.0±1.1	55.9±4.7	59.9±2.7
Furans	1.1±0.5	3.5±0.6	***	***	4.9±0.2	2.6±0.9	***	***
Ketones	10.4±0.9	6.7±2.5	***	***	6.5±1.6	8.3±0.5	***	***
Olefins	0.8±0.5	1.5±0.1	***	***	2.2±0.6	5.3±0.4	***	***
PAHs	1.9±0.5	4.8±1.6	33.3±1.1	32.9±2.9	3.3±0.9	5.5±1.6	29.6±4.6	26.6±0.7
Phenols	42.4±1.4	41.9±3.5	0.7±0.3	1.9±0.3	37.8±1.8	35.4±1.9	0.3±0.4	0.5±0.4

*** Not detected

2.3.3.2 Py-GC/MS - Aromatics carbon selectivity

The carbon selectivity (%) of aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene, benzene derivative, and PAHs) obtained from py-GC/MS was analyzed to understand the impact of co-pyrolysis conditions on the selectivity of aromatic hydrocarbons (shown in Figure 5). Carbon selectivity was defined as moles of carbon in a specific aromatic hydrocarbon compound divided by moles of carbon in total quantified selected aromatic hydrocarbons. Benzene derivatives (selectivity from 37.3 to 41.5%) dominated aromatics hydrocarbons compounds in the absence of catalyst at both temperatures (650 and 750°C). However, in the presence of catalyst (HZSM-5), benzene derivatives selectivity declined sharply to about 9.1% to 10.4% under all pyrolysis conditions. HZSM-5 considerably influenced carbon selectivity of ethylbenzene, xylene, and PAHs as depicted in Figure 5. As selectivity of ethylbenzene, xylene and PAHs sharply

increased from lowest of 4.4%, 4.6%, and 1.4%, to highest of 15.6%, 18.0% and 12.4%, respectively, in presence of catalysts. Benzene selectivity in non-catalytic under both methane and helium were higher than those in catalytic at the same temperature. Toluene selectivity in non-catalytic declined as temperature increased under helium atmosphere, while under methane it increased when temperature increased. HZSM-5 reduced benzene selectivity and increased toluene selectivity when compared with non-catalytic.

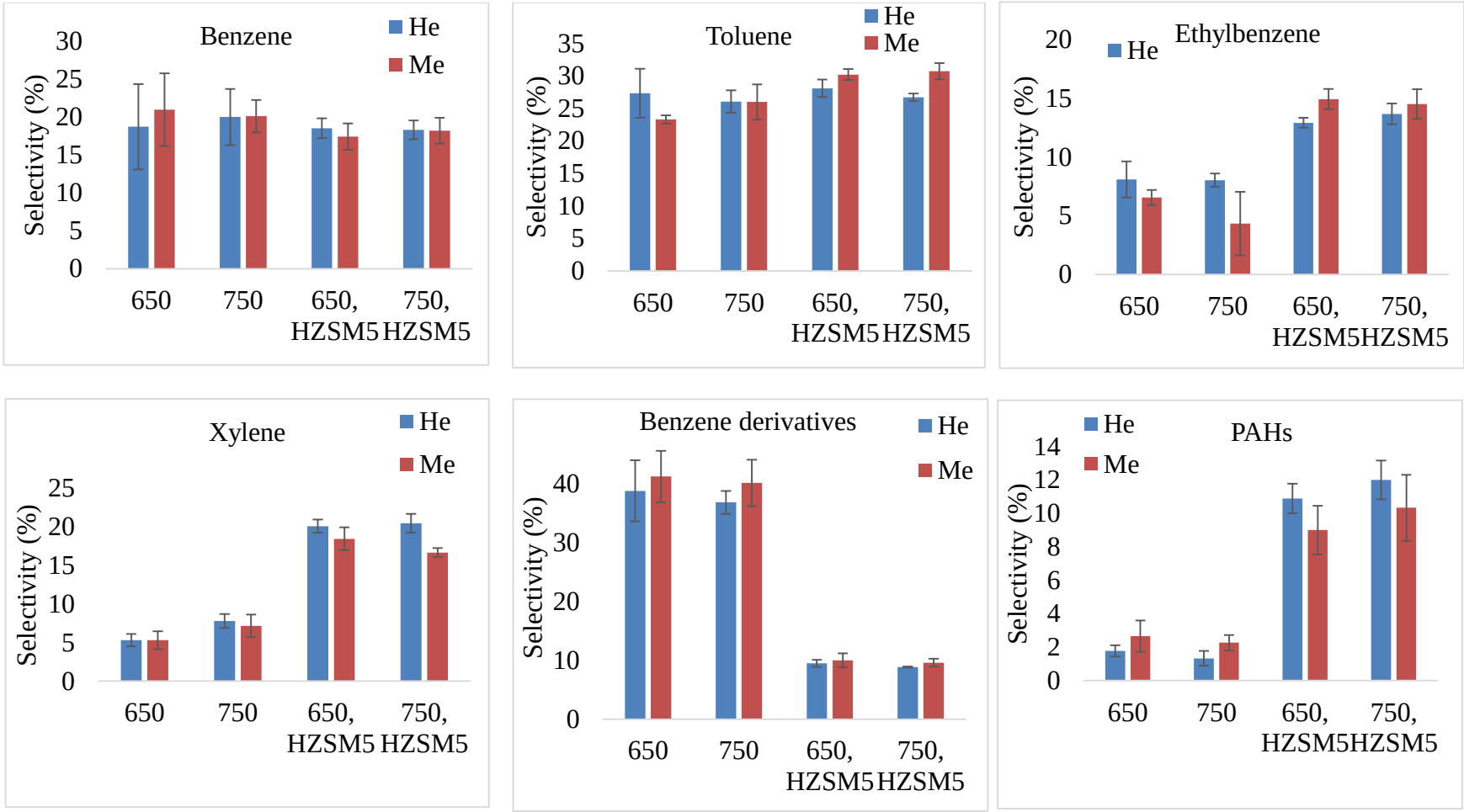


Figure 5. Aromatics selectivity (%) of py-GC/MS products obtained under methane (Me) and nitrogen (He) in catalytic and non-catalytic pyrolysis at 650 and 750°C..

2.4 Conclusion

Influence of methane on fast catalytic pyrolysis of eastern red cedar over MoZn/HZSM-5 and HZSM-5 catalysts at 650 and 750℃ were assessed in fixed bed reactor and Pyroprobe reactors. Maximum yield of bio-oil (about 53.4% on a weight basis) was achieved under methane over MoZn/HZSM-5 at 650℃. Highest energy content and yield of about 10.2 MJ/kg and 29.9%, respectively were both achieved under methane and same temperature of 650℃. Incorporation of methane in pyrolysis using a fixed bed improved yield of aromatics hydrocarbons to the maximum of about 56.8% (peak area) at temperature of 750℃ over MoZn/HZSM-5. The lowest yield (%) of oxygenated compound groups of acids (not detected), aldehydes (not detected), ketone (3.0%), and phenols (25.2%) were achieved when MoZn/HZSM-5 used under methane at 750℃. This demonstrated that MoZn/HZSM-5 was more effective in reducing oxygenated compounds compared to HZSM-5 only. Biochar yield was mainly influenced by temperature, as it decreased when temperature increased from 650 to 750℃. The yield of biochar was in the range of 21 to 26%wt. The results demonstrated that co-pyrolysis methane with eastern red cedar over MoZn/HZSM-5 improved aromatic hydrocarbons and bio-oil yield. However, further assessment of chemical and physical properties of bio-oil would be needed to fully understand reactive intermediates involved in the mechanism of catalytic co-pyrolysis of methane with biomass.

CHAPTER III

3 UPGRADE OF MUNICIPAL SOLID WASTE DERIVED BIO-OIL BY METHANE CO-PYROLYSIS OVER MoZn/HZSM-5 USING PYROLYSIS GC/MS

Abstract

In this study, fast pyrolysis of municipal solid waste using a pyrolysis-GC/MS was carried out at three temperatures (550, 650 and 750°C) and two catalysts (MoZn/HZSM-5, HZSM-5 and control) under methane and helium atmospheres. The effects of temperature, catalyst, and atmosphere on the chemical compositions and aromatic hydrocarbons yield of pyrolysis products were investigated. Bio-oil compositions were grouped in acids, alcohols, aldehydes, benzene derivatives, BTEXs, furans, ketones, olefins, PAHs, and phenols. While aromatics hydrocarbons consisted of benzene derivatives, BTEX and PAHs. Benzene derivative was mostly dominated by styrene. In non-catalytic condition, the dominant groups were benzene derivatives, BTEX, and olefins. Olefin and benzene derivative considerably reduced when both HZSM-5 and MoZn/HZSM-5 were used under both methane and helium at all temperatures. HZSM-5 and MoZn/HZSM-5 increased carbon selectivities of toluene, ethylbenzene, and xylene, while reduced those of benzene derivatives.

3.1 Introduction

The generation of municipal solid waste (MSW) is rapidly multiplied as the world's population grows with ever expanding urbanization and industrialization. The massive production of MSW is posing health hazards, environmental problems and challenges in waste management and handling all over the world [49]. MSW generation was about 1.3 billion metric tons worldwide in 2012 and predicted to reach 2.2 billion metric tons in 2025. Most of the MSW end up either in landfills or get burned, causing human health and environmental problems [50]. In the United States, about 254 million tons of MSW were generated in 2013. Recycling and composting recovered about 87 million tons, while the rest was either disposed of on landfills or burned [51]. Landfills are considered as one of the major contributors of anthropogenic greenhouse gases (GHG) emissions (CO_2, CH_4, N_2O). In 2004, landfills accounted for about 18% of global emissions of anthropogenic methane, which make up about 90% of total anthropogenic gases released from wastes a year [52].

Several thermochemical and other technologies (incineration, co-combustion, gasification, fast pyrolysis, anaerobic digestion for biogas recovery) have been employed to utilize MSW for energy recovery and tackle the issues associated with disposal and handling. These technologies have potential to mitigate problems and challenges associated with the disposal and management of MSW [52, 53, 54, 55]. Among these technologies, incineration is the most common and globally adopted [56]. However, incineration produces hazardous gases (such nitrous oxide), and air pollutant particulate matters and therefore requires an extensive purification to remove hazardous gases when compared to other technologies [57, 58]. On the other hand, fast pyrolysis possesses several

advantages over incineration and therefore a potential alternative to incineration. Fast pyrolysis produces chemicals and liquid biofuels (known as bio-oil) that are transportable. Whereas incineration mainly focuses on energy recovery through production of electricity and heat. Although advanced air pollutants control systems are available for modern incineration, these are expensive to implement because of high volume of pollutants generated.

Most studies on fast pyrolysis have focused on utilization of biomass as the feedstock, but MSW has various advantages over biomass to use as feedstock. For example in the USA, firms get paid for utilization of MSW main because of MSW landfills scarcity [59]. Unlike biomass, utilization of MSW does not directly compete with production of food. Production of biomass as feedstock for bioenergy products lead to clearing of forestland and grassland. With a projection of about 225 million dry tons biomass from forestland by 2030, large agricultural and forest land will be lost [60]. Unless production of biomass was grown on degraded and uninhibited agricultural lands, it will indirectly increase GHG emissions [61]. In contrasts, MSW is collected from landfills and this lead to a reduction of anthropogenic GHG emissions and freeing up land [62]. MSW will continue to be abundant since its generation is closely linked to the world‘s population, urbanization, and economic development of nations. Thus MSW is considered a potential to substitute biomass as feedstock for production of renewable energy.

Although fast pyrolysis of MSW is considered a promising and potential alternative to incineration, the bio-oil generated cannot be used directly due to its adverse properties of complex chemical composition, high water, and oxygen content, low pH, chemical instability and corrosiveness [63, 64, 65, 66]. These adverse bio-oil properties are result of

heterogeneous nature of MSW, which contains organic matters, plastics and inorganic matters [66, 67]. Bio-oil has been upgraded by incorporating catalyst either during fast pyrolysis or in secondary processes. However, these techniques suffered from incomplete removal of oxygen from bio-oil, coking and deactivation of catalysts used or use of expensive catalysts and hydrogen. Recently, employing methane in fast pyrolysis over catalyst is proposed to alleviate these problems of bio-oil without the need of expensive hydrogen [1, 2]. Use of methane, which is the main component of the abundant natural gas, will provide additional hydrogen important for deoxygenation and hydrogenation processes that upgrade bio-oil to desirable aromatics hydrocarbons. Since activation of methane requires high temperature [23, 24], modified bimetallic zeolite catalysts were used to both reduce methane activation temperature and facilitate selectivity of aromatics hydrocarbons formation. Their studies that used ZSM-5 loaded Zn reported that Zn facilitated activation of methane which ZSM-5 encouraged deoxygenation for bio-oil upgrading.

The purpose of this study was to employ methane in fast pyrolysis of MSW over molybdenum modified bimetallic (MoZn/HZSM-5) and HZSM-5 catalysts to investigate the enhancement of aromatic hydrocarbons yields that improve the quality of bio-oil generated from MSW. Fast catalytic co-pyrolysis of methane and MSW was carried out using pyrolysis gas chromatography/mass spectrometry (Py–GC/MS). Aromatics hydrocarbon products generated were identified.

3.2 Method and Materials

3.2.1 Materials

MSW pellets of 16 mm diameter were supplied by WastAway Inc., (Morrison, TN, USA). WastAway Inc collects MSW from various municipalities in the USA, and converts them into pellets after removing metals and inert materials (including ash from glass and rocks) [68]. These pellets were produced through screening, magnetic sorting (metals), shredding, steam hygienization and pellets compressing. The characteristic of MSW disposable in the USA cities were summarized in a fact sheet by US Environmental Protection Agency 2015 [51]. The ultimate and proximate analyses of the MSW were performed by Hazen Research, Inc. (Golden, CO, USA) (shown in Table 10). The properties of MSW pellets were compared to those of eastern red cedar and switchgrass that was previously used in our laboratory. The switchgrass and eastern red cedar have been extensively studied and reported in previous studies conducted in our laboratory at OSU [69, 70, 4]. The MSW pellets were ground using a mill fitted with a sieve of 150µm size to use the sample in pyroprobe.

The powder ZSM-5 Zeolite catalysts in the deprotonated state were purchased from Zeolyst International, (Pennsylvania, USA). ZSM-5 has characteristic of 30 molar ratio (SiO2/Al2O3) and 400 m^2 /g specific surface area. The ZSM-5 catalyst was calcined in an oven at 500°C for 6 h under air atmosphere to form protonated state of HZSM-5. HZSM-5 was then used for the synthesis of MoZn/HZSM-5 catalyst. MoZn/HZSM-5 was prepared in accordance with the procedure described in previous study [29].

Table 10. Properties of MSW pellets comparable with those of eastern red cedar and switchgrass previously used in our lab

	Parameter	MSW pellets	Eastern red cedar	Switchgrass
Ultimate Analysis (d.b. wt.%)	Carbon	58.79	55.14	51.66
	Hydrogen	7.10	5.88	5.95
	Nitrogen	0.16	0.20	0.32
	Sulfur	0.16	0.01	0.045
	Oxygen	33.80	38.77	42.03
Proximate Analysis (w.b. wt.%)	Moisture	3.84	10.39	7.69
	Ash	13.74	1.14	3.63
	Volatile	74.55	70.17	72.56
	Fixed carbon	8.39	18.3	16.12
High Heating Value (MJ/kg)		20.28	17.68	16.37
Low Heating Value (MJ/kg)		18.92	16.31	15.04

3.2.2 Fast pyrolysis GC/MS

Fast co-pyrolysis (non-catalytic and catalytic) of methane with MSW were conducted using a commercial analytical pyroprobe (model 5200, CDS Analytical Inc., Oxford, PA, USA) connected to an online gas chromatography (GC 7890A Agilent, CA, USA) coupled with mass spectrometry detector (MS 5975C Agilent, CA, USA). The pyroprobe consists of a probe filament rod to heat the sample at a specific heating rate, and an adsorbent trap (Tenax-TA^{TM}) to absorb condensable pyrolysis vapors. The pyroprobe was connected to a computer where pyrolysis conditions (pyrolysis temperature, heating rate, absorption and desorption temperatures, holding time and reactant gas option) were controlled. The GC/MS contained a DB-5 capillary column (30 mL × 0.32 mm internal diameter and 0.25 µm film thickness) for chromatographic separation. The fast co-

pyrolysis experiments were performed with a heating rate of 1000°C s^{-1} using about 0.3 mg of MSW sample and 3 mg of catalyst loaded in a quartz tube (25 mm length & 1.9 mm I.D.). Quartz wool was used to hold and separate MSW and catalyst in the quartz tube. Helium of 99.999% purity was used as a carrier gas at a flow rate of 40 ml/m while methane was used as a reactant gas. Reactant gas option on the pyroprobe was only enabled in fast co-pyrolysis under methane atmosphere and remained disabled in helium atmosphere. The pyrolysis vapors were carried to a Tenax-TA™ for absorption of condensable vapors at 45°C and desorption at 300°C. The desorbed volatiles from a Tenax-TA™ was carried to GC column by carrier gas via transfer line kept at temperature of 300°C. The GC was working in a split mode with a split ratio of 30:1 (split vent flow to column flow). Compounds in the pyrolysis products were separated in the DB-5 capillary column and identified by MS detector. The initial temperature of the GC column oven was 40°C held for 2 min, and increased by the heating rate of 5°C to 208°C and held at that temperature for 20 min. MS detector used electron ionization techniques to identify bio-oil compounds in full scan range of 30 to 500 m/z. National Institute of Standards and Technology (NIST) mass spectral library data was used to identify the compounds peaks. Compounds of interest were quantified based on calibration of standard organic compounds. Semi-quantitation was also carried out according to the relative peak area of compounds.

3.2.3 Experimental design

The experiment was designed to evaluate the effects of catalyst (MoZn/HZSM-5, HZSM-5 and non-catalytic) and temperature (550, 650, 750°C) on bio-oil derived from fast co-pyrolysis of methane and MSW. A full factorial design with three factors

(catalyst, temperature, and pyrolysis atmosphere) was performed and results were statistically analyzed using SAS version® 9.4.

3.2.4 Analysis of fast pyrolysis GC/MS products

Peak areas of the bio-oil compounds with quality values of at least 80% were analyzed individually. The compounds were categorized based on their functional groups of acids, alcohols, aldehydes, benzene derivatives, BTEX (benzene, toluene, ethylbenzene, and xylene), furans, ketones, olefins, phenols and PAHs (polyaromatic hydrocarbons). Total peak areas of these groups were used to elucidate their yields as effected by treatments. To evaluate effects of aromatic hydrocarbon yields in the bio-oil, selected aromatics hydrocarbons (BTEX, benzene derivatives, and PAHs) were quantified and their carbon yields were determined. Carbon selectivity of aromatics hydrocarbons was determined by dividing moles of carbon in the specific compound by moles of carbon in all quantified compounds.

3.3 Results and discussion

3.3.1 MSW characteristic analysis

Table 10 shows the ultimate and proximate analysis of MSW compared with those of eastern red cedar and switchgrass. Characteristics of MSW have some similarities to eastern red cedar and switchgrass previously used in our lab. However noticeable difference was observed in oxygen, moisture, ash, fixed carbon, and energy content. MSW has relatively lower oxygen, fixed carbon and moisture content and higher energy content as compared to the eastern red cedar and switchgrass. This may due to the presence of plastics that has lower moisture and high carbon contents. Formation of oxygenated compounds during a typical fast pyrolysis is mainly due to the high presence of oxygen

content of the feedstock. Oxygenated compounds and water content reduce the energy density of bio-oil, thus low oxygen and moisture contents of feedstock are beneficial to generate bio-oil with less adverse properties.

Constituents and properties of the MSW pellets were obtained from the literature. Robinson et al., (2017) estimated the constituents of the MSW pellets obtained from WastAway Inc., using a thermos-gravimetric technique. The authors reported that the MSW comprised of cellulosic materials (48.1 to 61.5 dry wt.%) and plastics (12.6 and 42.5 dry wt.%) [71]. This estimation was in agreement with Environmental Protection Agency (EPA) report 2013 that representative MSW generated in the US consists of plastics and cellulosic material sources (papers, food, wood, and yard trimmings) in the amount of 12.8% and 61.3%, respectively [51]. The MSW pellets from WastAway Inc., were studied in a co-gasification with woody biomass using an air-blown bubbling fluidized bed [72].

3.3.2 Chemical composition of fast pyrolysis-GC/MS products

Table 11 presents a list of major compounds identified by online GC/MS analysis of the condensable vapors from pyrolysis of MSW. Compounds are listed together with their functional groups and chemical formula. Styrene was the most abundant compound of benzene derivatives under all pyrolysis conditions. High presence of styrene in bio-oil was mainly derived from pyrolysis of polystyrene plastic found in the MSW. By pyrolyzing several plastic types, Miland et al., (2017) found that bio-oil derived from polystyrene plastic contained 48.3% of styrene which was dominant among compounds investigated [73]. Phenol groups were mostly made up of phenol, phenol, 2-methyl- and phenol, 3-methyl- in non-catalytic, but these were reduced or not detected when MoZn/HZSM-5 or HZSM-5 was used. BTEX group was largely dominated by toluene and benzene in non-catalytic under both methane and helium; however, ethylbenzene and xylene slightly increased in the presence both catalysts.

Table 11. Major compounds detected in pyrolysis products of MSW

Group	Major Compounds	Formula
Acids	n-Hexadecanoic acid	$C_{16}H_{32}O_2$
	cis-Vaccenic acid	$C_{18}H_{34}O_2$
	Octadecanoic acid	$C_{18}H_{36}O_2$
	1,4-Benzenedicarboxylic acid, ethyl methyl ester	$C_{11}H_{12}O_4$
Alcohol	1,2-Benzenediol, 3-methoxy-	$C_7H_8O_3$
	1,2-Benzenediol, 4-methyl-	$C_7H_8O_2$
	1,3-Benzenediol, 4-ethyl-	$C_8H_{10}O_2$
	1,14-Tetradecanediol	$C_{14}H_{30}O_2$
Aldehyde	Benzaldehyde	C_7H_6O
	2-Furancarboxaldehyde, 5-methyl-	$C_7H_6O_2$
Benzene derivatives	Benzene, 2-propenyl-	C_9H_{10}
	Benzene, propyl-	C_9H_{12}
	Benzene, 1-ethyl-2-methyl-	C_9H_{12}
	Benzene, 1,2,3-trimethyl-	C_9H_{12}
	Indane	C_9H_{10}
	Indene	C_9H_8
	Styrene	C_8H_8
	2-Methylindene	$C_{10}H_{10}$
	.alpha.-Methylstyrene	C_9H_{10}
BTEX	Benzene	C_6H_6
	Toluene	C_7H_8
	Ethylbenzene	C_8H_{10}
	Xylene	C_8H_{10}
Furan	Furan, 2,5-dimethyl-	C_6H_8O
	2(3H)-Furanone, 5-methyl-	$C_5H_6O_2$
	Furfural	$C_5H_4O_2$
Ketone	1,2-Cyclopentanedione	$C_5H_6O_2$
	1,2-Cyclopentanedione, 3-methyl-	$C_6H_8O_2$
	Acetophenone	C_8H_8O

Olefin	3-Heptene, 4-methyl	C_8H_{16}
	1,11-Dodecadiene	$C_{12}H_{22}$
	1-Pentadecene	$C_{15}H_{30}$
	1,19-Eicosadiene	$C_{20}H_{38}$
PAHs	Naphthalene	$C_{10}H_8$
	Naphthalene, 1-methyl-	$C_{11}H_{10}$
	Naphthalene, 2-methyl-	$C_{11}H_{10}$
	Naphthalene, 1-ethyl-	$C_{12}H_{12}$
	Naphthalene, 2,6-dimethyl-	$C_{12}H_{12}$
	Naphthalene, 1,5-dimethyl-	$C_{12}H_{12}$
	Phenanthrene	$C_{14}H_{10}$
	Phenanthrene, 2-methyl-	$C_{15}H_{12}$
Phenols	Phenol	C_6H_6O
	Phenol, 2-methyl-	C_7H_8O
	Phenol, 3-methyl-	C_7H_8O
	p-Cresol	C_7H_8O
	2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$
	Phenol, 2-(phenylmethoxy)-	$C_{13}H_{12}O_2$

Discussions of the results is mainly focused on the qualitative analysis of chemical compositional. Quantitation analysis was limited to the selected compounds (aromatics hydrocarbons) of the bio-oil products. Fast pyrolysis bio-oil have complex chemical compositions comprised of organic compounds of several functional groups. Figure 6 depicts the effects of methane, temperature and catalysts on the chemical compositional characteristic of the MSW derived bio-oil. Chemical compositions were summed in terms of peak area (%), which corresponds to the relative amount of each compound (functional) group in the bio-oil. Functional groups analyzed in bio-oil were acids, alcohols, aldehydes, benzene derivatives (BD), BTEX, furan, ketone, olefin, PAHs, and phenols (with a match

quality value of <85%). In non-catalytic conditions, olefins together with benzene derivatives, and BTEX were dominant groups at all temperatures. However, under helium, olefins were the most dominant at all three temperatures accounting for 28.9%, 33.9% and 44.9% peak area at 550, 650 and 750°C, respectively. Under methane, benzene derivatives accounted for 25.9% and 40% peak area at high temperature of 650 and 750°C, respectively, and olefin dominated at the lowest temperature of 550°C.

In catalytic fast pyrolysis under both methane and helium, BTEX dominated the compounds accounting for about 63.2% to 79.7%. The highest yield of BTEX was obtained under helium over MoZn/HZSM-5 at 550°C. BTEX with benzene derivatives and PAHs account for more than 95% of total peak areas of products detected in catalytic conditions at all three temperatures. Under helium, BTEX decreased as temperatures increased over both catalysts. While under methane, BTEX increased as temperature increased over MoZn/HZSm-5 catalyst. At low temperature of 550°C, introducing of methane did not increase peak area of BTEX under both catalysts. However, at high temperature 650°C and 750°C, BTEX increased over both catalysts. This may indicate that activation of methane over the catalyst is efficient at only at high temperatures.

Unsaturated hydrocarbons, such as olefins, were observed abundantly in non-catalytic fast pyrolysis of MSW under both methane and helium. However, olefins were reduced and in some case not detected in the presence of both catalysts. It was evident that formation of oxygenated compounds, such as acids, alcohols, aldehydes, furan derivatives, ketones, and phenols, occurred more in non-catalytic fast pyrolysis than catalytic fast pyrolysis. Oxygenated compounds decreased rapidly or were not detected when both HZSM-5 and MoZn/HZSM-5 were introduced in the fast pyrolysis. These results

demonstrated that presence of the two catalysts facilitated deoxygenation of volatiles. The decreases in oxygenated compounds in the presence of catalysts were consistent with results of a previous study [10]. The authors found that oxygenated compounds, such as phenol, benzene 1,3-diol, and methyl-phenol, accounted for more than 50% of non-catalytic pyrolytic bio-oil obtained from refuse derived fuels and the amount reduced by about 30 - 45% in presence of Y-zeolite, Ni–Mo and ZSM-5 catalysts.

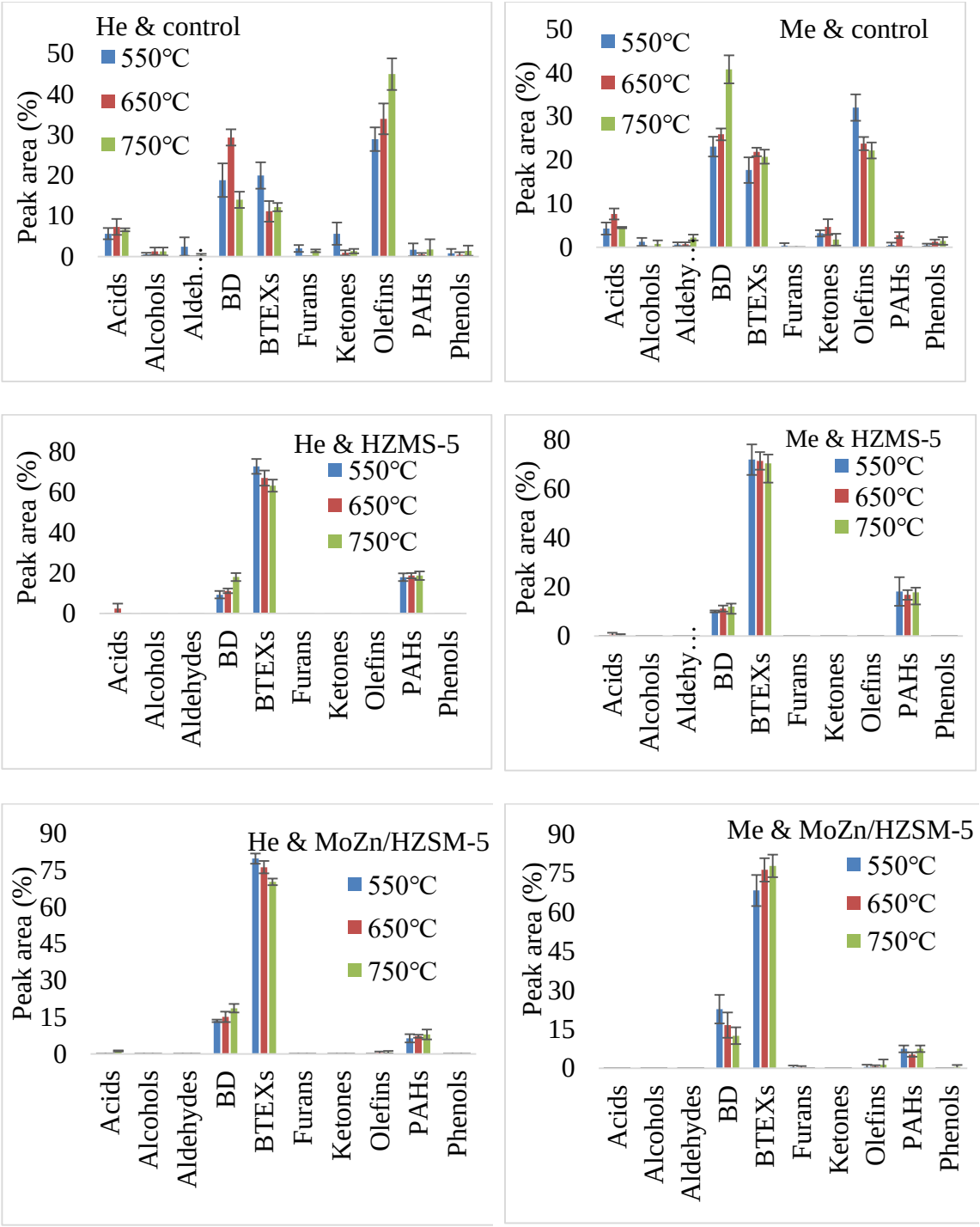


Figure 6. Chemical composition (peak area %) of MSW pyrolysis-GC/MS products as influenced by temperature and catalyst under helium (He) and methane (Me).

Zeolite based catalysts were introduced in fast co-pyrolysis of methane and MSW to promote methane activation and deoxygenation for more formation of aromatic hydrocarbons. The properties of zeolite (acidity and pore size) facilitated aromatics hydrocarbons selectivity and yield, and deoxygenation during fast pyrolysis. Effects of zeolite catalysts have been extensively studied in fast pyrolysis of mainly lignocellulose biomass and as well as of waste plastics [11, 67]. Carbon yield (%) distribution of BTEX, benzene derivatives, and PAHs are presented in Table 12. In non-catalytic pyrolysis, total carbon yield of hydrocarbons ranges from about 37.0% to 39.8% of the total of carbon yield of bio-oil (quantified compound). The yield increased to a maximum of about 59.8% under methane over MoZn/HZSM-5 catalyst at 650℃. High yields of BTEX was also achieved under methane in presence of MoZn/HZSM-5 at 750℃. Unlike biomass, MSW contains a large fraction of plastics (PS, PP, PE, and PET). Presence of plastics in the feedstock increased both yield and selectivity of aromatic hydrocarbons of bio-oil. Several studies reported yield of more than 90% wt from pyrolysis of different plastics [74, 75, 76]. Pyrolysis of mixed plastics and polyolefin at a temperature higher than 650℃ produced mainly aromatics hydrocarbons (benzene, toluene, styrene, and naphthalene) [77]. However, it was demonstrated elsewhere [78, 79, 80] that pyrolysis of plastics with biomass rich reduces both yields and aromatics.

Table 12. Total carbon yield (%) of BTEX, benzene derivatives and PAHs from fast co-pyrolysis over three different temperatures.

Treatment	He, Control			He, HZSM-5			He, MoZn/HZSM-5		
	550°C	650°C	750°C	550°C	650°C	750°C	550°C	650°C	750°C
BTEXs	17.7±1.2	15.0±1.6	21.6±1.1	40.1±1.3	42.9±1.9	38.1±1.8	41.6±4.9	43.8±2.3	41.0±0.9
Benzene derivatives	18.5±0.8	21.5±2.2	16.3±1.3	10.3±1.7	8.3±0.6	6.1±2.3	9.3±0.8	5.4±1.9	4.9±1.8
PAHs	1.5±0.3	0.0±0.4	1.2±0.8	6.6±0.6	6.9±0.1	7.3±1.1	5.2±0.9	5.7±1.3	7.2±0.9
Total	37.6	37.4	39.0	56.9	58.1	51.5	56.1	54.9	53.2
	Me, Control			Me, HZSM-5			Me, MoZn/HZSM-5		
Treatment	550°C	650°C	750°C	550°C	650°C	750°C	550°C	650°C	750°C
BTEXs	17.4±2.9	18.1±2.1	16.1±1.8	41.2±2.3	42.8±3.0	39.7±2.9	39.2±1.7	44.3±1.9	45.9±2.8
Benzene derivatives	18.1±1.7	19.5±0.8	22.9±1.1	5.4±0.5	5.66±1.1	5.7±0.9	10.2±2.3	9.3±1.8	5.9±1.3
PAHs	1.5±0.0	1.05±0.3	0.8±0.2	9.11.9	8.7±1.12	7.1±1.8	4.0±0.4	6.3±0.1	4.4±0.8
Total	37.1	38.7	39.8	55.7	55.1	52.4	53.5	59.8	56.2

3.3.3 Aromatics hydrocarbons selectivity

Carbon selectivity of aromatics hydrocarbons of benzene, toluene, ethylbenzene, xylene, benzene derivatives, and PAHs are presented in Figure 7. Selected aromatics hydrocarbons were quantified to investigate the effect of treatments on the carbon distribution of these important compounds in the petrochemical industries. The catalyst was the most factor influenced the carbon selectivity of all selected aromatics hydrocarbons as shown in Table 13. The temperature had significant effects on benzene and benzene derivatives. Toluene, ethylbenzene, and xylene increased significantly in presence of both MoZn/HZSM-5 and HZSM-5 catalysts. While benzene derivatives were significantly reduced in catalytic pyrolysis compared to non-catalytic. HZSM-5 was more effective in the formation of PAHs compared to MoZn/HZSM-5 under both methane and helium at all temperatures (650 and 750°C). Although the main effects of temperature and catalyst were significant on benzene and benzene selectivity, their interactions were also significant, signifying that their effects depended on the level of each other. To elucidate the unique effects of interactions of catalyst and temperature on the carbon selectivity of benzene, mean values were investigated as presented in Table 14 and 15. MoZn/HZSM-5 performed greatly at 550 and 650°C with a mean benzene selectivity of 31.1 and 32%, while HZSM-5 was superior at 750°C, with mean selectivity of 30.1%. For atmosphere and catalyst interaction effects on benzene selectivity, methane increased benzene selectivity effectively over MoZn/HZSM-5 (30.4%) and in non-catalytic (39.5) compared to helium, but it was inferior over HZSM-5 (27.9%).

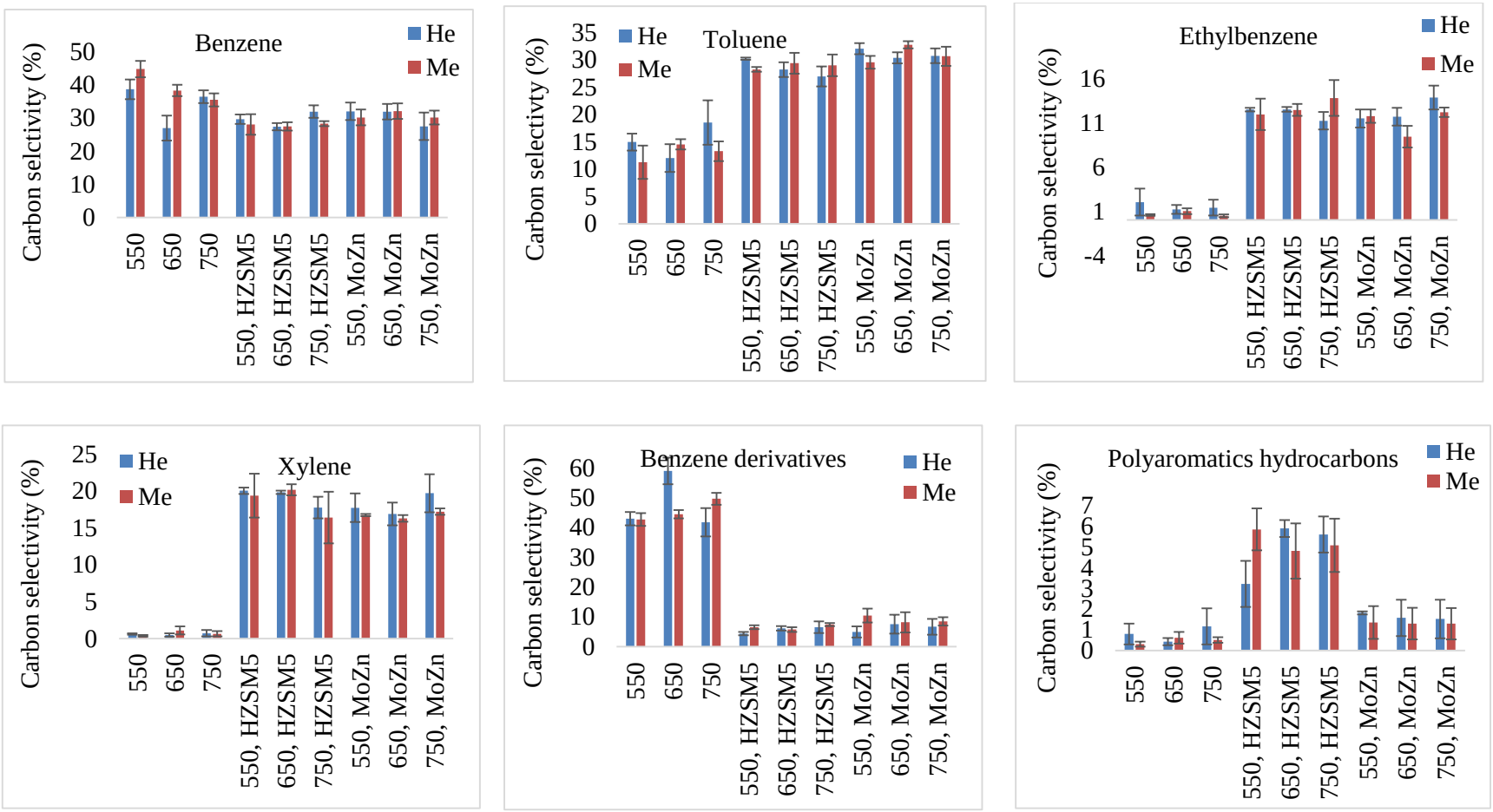


Figure 7. Effect of catalyst (Control, HMZS-5 & MoZn/ZSM-5) on aromatics selectivity of fast co-co-pyrolysis of methane and MSW at three temperatures (550, 650 & 750°C).

Table 13. Effects (p-values) of temperature, atmosphere, catalyst and their interaction on carbon distribution of aromatics hydrocarbons

	Temp	Atm	Cat	Temp* Atm	Temp* Cat	Atm*Cat	Temp* Atm*Cat
Benzene	0.0082	0.0995	<.0001	0.0808	0.001	0.0028	0.0511
Toluene	0.8464	0.3953	<.0001	0.028	0.2816	0.297	0.3594
Ethylbenzene	0.2002	0.1806	<.0001	0.6011	0.1031	0.0794	0.113
Xylene	0.735	0.2129	<.0001	0.4925	0.024	0.4662	0.9833
Benzene derivatives	0.007	0.5939	<.0001	0.0002	0.0027	0.0415	0.0003
PAHs	0.6436	0.7105	<.0001	0.236	0.6876	0.5211	0.0621

Temp, Atm, Cat stand for temperature, atmosphere, and catalyst respectively.

Significant differences were considered at p-value of less than 0.05

Table 14. Effects of interations of three factors (catalyst vs. temperature vs. atmosphere) on the carbon selectivity (%) of benzene and benzene derivatives (MSW py-GC/MS)

Selectivity (mean %)	Treatment conditions	Helium			Methane		
		550°C	650°C	750°C	550°C	650°C	750°C
Benzene	Control	38.7±3.6	26.9±4.6	36.5±2.4	44.7±3.1	38.3±2.1	35.5±2.4
	HZSM5	29.7±1.8	27.4±1.3	31.9±2.3	28.1±3.8	27.5±1.5	28.3±0.9
	MoZn/HZSM5	32.0±3.2	31.9±2.9	27.5±5.1	30.1±2.9	32.1±2.8	30.2±2.5
Benzene derivatives	Control	42.9±2.7	58.9±5.4	41.7±5.8	42.7±2.6	44.4±1.7	49.6±2.5
	HZSM-5	4.4±0.7	6.2±0.9	6.5±2.4	6.5±0.8	5.8±1.0	7.5±0.6
	MoZn/HZSM5	4.9±2.3	7.6±3.8	6.7±3.2	10.5±2.8	8.2±4.1	8.5±1.7

Table 15. Effects of interactions of two factors (catalyst vs. temperature and catalyst vs. atmosphere) on the carbon selectivity (%) of benzene and benzene derivatives (MSW py-GC/MS)

Selectivity (mean %)	Catalyst	Temperature			Atmosphere	
		550℃	650℃	750℃	Helium	Methane
Benzene	Control	41.7±4.4	32.6±7.0	35.9±3.9	34.0±6.3	39.5±4.6
	HZSM5	28.9±2.8	27.4±1.3	30.1±2.6	29.7±2.5	27.9±2.1
	MoZn/HZSM5	31.1±2.9	32.0±2.5	28.8±2.2	30.5±4.0	30.8±2.5
Benzene derivatives	Control	42.8±2.3	51.8±8.7	45.6±5.8	47.8±9.3	45.5±3.7
	HZSM5	5.4±1.3	6.0±0.8	7.0±1.6	5.7±1.7	6.6±1.0
	MoZn/HZSM5	7.7±3.8	7.8±3.6	7.6±2.5	6.4±3.0	9.1±2.9

3.4 Conclusion

Pyrolysis GC/MS was employed to analytically investigate fast pyrolysis of MSW with methane over molybdenum modified (MoZn/HZSM-5) and HZSM-5 catalysts for the upgrading of bio-oil. The addition of methane over catalyst slightly increased total carbon yields of aromatics hydrocarbons over high temperature of 650 and 750℃. The highest carbon yield of aromatics hydrocarbons was about 59.8% over MoZn/HZSM-5 at 650℃, an increase from maximum of 39.8% achieved under non-catalytic pyrolysis. MoZn/HZSm-5 catalyst was more effective in the formation of aromatic hydrocarbon under methane at high temperature when compared with non-modified HZSM-5. Furthermore, the results indicate that the catalysts significantly influenced the selectivity of aromatic compounds. Both catalysts (MoZn/HZSM-5 and HZSM-5) increased selectivities of toluene, ethylbenzene, and xylene production, while decreased benzene derivatives. This analytical study demonstrated that methane over MoZn/HZSM-5 and HZSM-5 improved aromatic hydrocarbons of MSW derived bio-oil.

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