Journal of Materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 5, Page 1617-1625

http://www.jmaterenvironsci.com/

Design of Experiment and Upgrading of Pyrolysis Vapors Using ZrO_2-TiO_2, ZSM-5, and Silica Catalysts

M.A. Behrens[*], H. Akasaka, N. Ohtake, J.S. Cross

Department of Mechanical Engineering, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro, Tokyo 152-8552, Japan

Received 24 Oct 2016,
Revised 21 Jan 2016,
Accepted 27 Jan 2017

Keywords

- ✓ Pyrolysis;
- ✓ Catalyst;
- ✓ Bio-oil;
- ✓ ZrO_2-TiO_2;
- ✓ ZSM-5

M.A. Behrens
behrens.m.aa@m.titech.ac.jp
+81357343723

Abstract

Biomass can be converted to bio-oil, a promising carbon neutral energy source. In this work, bio-oil quality and quantity were optimized by utilizing a fixed-tube reactor's temperature, wood pellet size, and nitrogen flow rate in a central composite experimental design. The highest bio-oil yield (37%±1.3%) and % alkane + aliphatic area from H-NMR (57%±1%) occurred with a temperature of 550°C and low N_2 flow rate. ZrO_2-TiO_2 catalyst, silica catalyst, and ZSM-5 catalyst were tested for upgrading bio-oil. The % alkane + aliphatic area from H-NMR at the same operating conditions were as follows for aqueous-phase bio-oil; uncatalyzed (56%±0.2%), silica bead (56%±1%), ZSM-5 (63%±1%) and ZrO_2-TiO_2 (62%±1%). The major result of this work confirms the different effects between ZSM-5 and ZrO_2-TiO_2 catalyst. ZSM-5 catalyst doubled the amount of aromatics in the organic-phase of the bio-oil from 8% to 17% as measured by GC-MS area while ZrO_2-TiO_2 catalyst increased the cyclopentanones from 3% to 10%. From our analysis, ZSM-5 is the better catalyst for upgrading pyrolysis vapors as it decreases the oxygen containing compounds which is expected to increase the heating value of the bio-oil.

1. Introduction

A steep rise in the demand for fossil fuels due to increasing industrialization of countries around the world has led to a need for an alternative fuel source. Developed societies need oil and other energy sources for fueling cars, homes, living, and heating. The increased depletion of fossil fuels and rise in energy consumption steered research focus on to renewable, sustainable, and cost effective energy sources [1], [2]. Biofuels are environmentally renewable, biodegradable, and generate acceptable quality exhaust [3]. Additionally, biomass is the only renewable carbon containing feedstock that can be used for the synthesis of hydrocarbon transportation fuels [4]. Pyrolysis is highly efficient with a bio-oil yield up to 70%, low capital investment and distributed production [5]. However, due to high oxygen content, the bio-oil from pyrolysis is acidic, has low energy density, and degrades over time.

For commercial use, the bio-oil must be upgraded. There are many different ways to upgrade bio-oils including hydrogenation, hydrodeoxygenation, catalytic pyrolysis, catalytic cracking, steam reforming, molecular distillation, supercritical fluids, esterification and emulsification [6]. Catalytic methods are beneficial because they can easily be added onto existing commercial infrastructure. Additionally, working with hydrogen at elevated pressures is unnecessary. The purpose of catalytic pyrolysis is to deoxygenate the pyrolysis vapors in order to decrease the bio-oil acidity and increase the bio-oil energy content and stability. Before bio-oil can be used as additives for conventional fuels, an efficient and economical upgrading method needs to be developed.

Many catalysts have been tested for upgrading pyrolysis vapors. The structure of the catalyst and chemical constituents affects the product of the pyrolysis due to size exclusion and catalyst acidity. A recent paper by Shantanu et al. found that mesoporous catalysts exhibiting high pore volume and acidity gave high gas and coke yields, while ZSM-5 was promising for creating aromatics [7]. Qiang Lu et al. studied three different commercial meso and macroporous catalysts (TiO_2 (Rutile), TiO_2 (Anatase) and ZrO_2-TiO_2) for upgrading pyrolysis vapors [8]. They found that ZrO_2-TiO_2 was most effective by increasing the hydrocarbon content from 0.1% to 13.1%. Additionally, S.D. Stefanidis et al. tested many catalysts and concluded that zirconia/titania and

ZSM-5 catalysts are the most interesting materials due to high surface area which reduces oxygen and increases aromatic content [9]. A direct, systematic comparison is important in order to understand the effects of the catalysts with the same experimental set-up and to determine which catalyst results in a higher-quality bio-oil. A blank silica catalyst, which is not expected to have any effect on the pyrolysis vapors, will also be used to confirm the bio-oil analysis methods.

In this work, an electrically heated furnace-based pyrolysis system was first calibrated using a central composite experimental design. The central composite design of experiments was conducted to optimize the fixed-tube reactor's temperature, wood pellet size, and nitrogen flow rate. Also, a better understanding of the relationship between the various process parameters affecting bio-oil quality, bio-oil quantity, and char was achieved. Next, different catalysts (ZrO_2-TiO_2, ZSM-5 and silica) were used to upgrade Japanese cypress wood chips' pyrolysis vapors. It is expected that ZrO_2-TiO_2 and ZSM-5 will upgrade the bio-oil due to the catalytic surface metallic sites. The research aim is to explore the different effects the catalysts have on the bio-oil composition and to decrease the oxygen content of the bio-oil.

2. Experimental details

2.1. *Materials*

The biomass feed consisting of Hinoki (Japanese Cypress) woodchips was supplied by Woodchip Garden, Tokyo, Japan [10]. The biomass material was sieved through 2.8 mm, 5.0 mm, and 9.5 mm sieves to obtain three different particle sizes (0-2.8 mm, 2.8 – 5.0 mm, and 5.0 – 9.5 mm). Elemental analysis was performed on the Hinoki wood using a Yanaco CHN corder MT-6 elemental analyzer and the results are as follows: C (46%), H (6%), N (0.1%), and by mass balance O (48%).

The ZrO_2-TiO_2 (40% Anatase TiO_2) was supplied by Saint Gobain NorPro and the silica beads (CARiACT Q-15) were supplied by Fuji Silysia Chemical LTD. The ZSM-5 (890 HOA) was supplied by Tosoh Corporation. Catalysts and wood were dried in an oven at 80°C overnight before use.

Table 1: The catalyst properties used in this study

Catalyst	Pore Size (nm)	Surface Area (m^2/g)
ZrO_2-TiO_2	11, 16, and 121	86.8
Silica	16.1	203
ZSM-5	0.58	310

2.2. *Experimental methods*

A central composite design of experiments was conducted to optimize the fixed-tube reactor's temperature, wood pellet size, and nitrogen flow rate for producing higher quality bio-oil. The center point was repeated three times to measure the system error as well as test for curvature with the dependent variables [11]. The software RcmdrPlugin.DoE package within the R environment (version 3.1.3) was used to perform the appropriate statistical analysis [12]. Table 2 below shows the design parameters. After finishing the central composited design and optimizing the reactor parameters, catalyst testing was conducted.

Table 2: Central composite design process parameters

DOE Factor	(x1) Temperature °C	(x2) N_2 Flow rate (L/min)	(x3) Particle size (mm)
-1	350	0.5	0-2.8
0	450	1	2.8-5.0
1	550	1.5	5.0-9.5

In general, catalyst (12 g) and Hinoki (12 g) were loaded into the 50 mm diameter quartz pyrolysis reactor and separated with glass wool. The reactor was purged with nitrogen for 5 minutes. Afterwards, the pyrolysis reactor was heated to the target temperature (350°C – 550°C) and the pyrolyzed vapors were carried by the nitrogen to the condensers. The large diameter reactor and wood's large particle sizes results in slower heating of the biomass. Hence, this set-up resembles a slow pyrolysis system rather than a fast pyrolysis system.

While slow pyrolysis has a reduced bio-oil yield, a fixed bed reactor is often used due to the easy set-up and can be used to compare different catalysts. The vapors were then condensed in a flask chilled using an ice bath. The resulting bio-oil was collected and analyzed.

2.3. *Analysis methods*

2.3.1. *H-NMR methods for bio-oil*

Proton nuclear magnetic resonance (H-NMR) was used to measure the bio-oil quality for the central composite design as well as for the catalyst tests. 10 µL of sample were dissolved in 700 µL of $CDCl_3$ solvent of 99.8% purity. The solvent signal $CDCl_3$ at 7.25 ppm was used as the reference for the samples. Samples were analyzed on the Bruker Biospin Avance III at 400 MHz using 16 transients. All samples were conducted in at least duplicate. Samples were retested if standard deviation of the integrated area exceeded 3.0%.

The proton shift of the H-NMR can determine the functional groups found in the bio-oil sample. By integrating the resultant curve, the % protons in the bio-oil associated with the functional groups can be determined. The chemical shift was assigned as shown in Figure 1 in the results section [13]. The water peak at 4.8 – 4.9 ppm and the solvent peak at 7.25 ppm are removed from the integration during the analysis by using ACD/Labs software [14]. The bio-oil quality was determined by adding the integrated areas of the alkane and aliphatic groups.

2.3.2. *GC-MS methods for bio-oil*

The compounds in the bio-oil were qualitatively analyzed with GC-MS. GC-MS was conducted on all catalyzed bio-oil samples. The samples were prepared as a 5% mixture of bio-oil with acetone.

The analysis was performed using a GC-2010 Plus equipped with GC-MS-QP2010 SE mass detector made by Shimadzu. A 30 m x 0.25 mm, 0.25 µm film thickness Rtx-5MS column was used with a 5 to 1 split entry. The initial oven temperature was held at 40°C for 10 minutes. It was then ramped to 50°C at 1°C/min and ramped to 130°C at 2°C/min. Finally the temperature was ramped to 300°C at 4 °C/min and held for 15 minutes. The bio-oil compounds were identified using the NIST 11 MS library and considered a successful match if the similarity was over 80. All experiments were conducted multiple times to confirm the consistency of the results.

3. Results and discussion

3.1. Design of experiment (DOE) results

The temperature was varied between 350°C and 550°C. The nitrogen flow rate was varied between 0.5 L/min and 1.5 L/min. The particle size was divided into three sections between 0-9.5 mm. The results of the 11 experiments are shown below in Table 3.

Table 3: Central composite design results

Run	**Factors**			**Bio-oil Yield**	**Char (g)**	**alkane + aliphatic area from H-NMR**
	x1 (Temp)	x2 (N_2 Flow)	x3 (Particle size)			
1	0	0	0	33 %	2.64	51%
2	-1	-1	1	33 %	3.18	53%
3	1	1	1	31 %	2.47	51%
4	1	-1	1	37 %	2.55	57%
5	1	1	-1	28 %	2.40	51%
6	0	0	0	33 %	2.68	54%
7	-1	1	1	26 %	3.20	49%
8	1	-1	-1	33 %	2.47	55%
9	-1	-1	-1	35 %	3.14	54%
10	-1	1	-1	26 %	3.05	51%
11	0	0	0	35 %	2.60	55%

From Table 3 it can be seen that the highest bio-oil yield occurs when nitrogen flow is low. Hence, nitrogen flow seems to strongly affect the bio-oil yield. However, the char amount does not seem to show a clear pattern with nitrogen flow. Rather, it appears to have a strong correlation with temperature. When temperature is -1 (350°C), the amount of char is the highest. The trend of % alkane + aliphatic area from H-NMR with independent variables is more difficult to perceive than bio-oil yield and char. Linear regression was conducted on the data to determine significant factors according to Equation 1 where y is the yield, char or % alkane + aliphatic area from H-NMR, x is the three independent factors and ε is the error.

$$y = \beta_0 + \sum_{j=1}^{k} (\beta_j x_j) + \sum_{i<j} \sum \beta_{ij} x_i x_j + \varepsilon \qquad (1)$$

Table 4 shows the independent parameters. The p-value evaluates the statistical significance of the model term. In this experiment, a p-value of <0.05 was determined to be significant [11]. The significant terms are highlighted in Table 4.

Table 4: Statistical results for central composite design

Response	β_0	β_1 **(Temp)**	β_2 **(N_2 Flow)**	β_3 **(Particle Size)**	β_{12}	β_{13}	β_{23}	**Curve**	R^2_{adj}
Char Yield	2.76	-0.33	-0.03	0.04	-0.01	-0.01	0.01	0.17	0.98
p-value	0.00	**0.00**	0.58	0.39	0.86	0.91	0.83	**0.02**	
Bio-oil Yield	0.32	0.01	-0.03	0.01	0.01	0.01	0.00	-0.02	0.88
p-value	0.00	0.19	**0.01**	0.31	0.36	0.14	0.85	0.13	
% Alkane + Aliphatic Area from H-NMR	0.53	0.01	-0.02	0.00	0.00	0.01	0.00	-0.01	0.57
p-value	0.00	0.19	**0.02**	0.83	0.54	0.32	0.54	0.67	

The regression coefficients and intercept are shown above Table 4 for the three dependent variables of char, bio-oil yield, and bio-oil quality. As was observed from the data, temperature affects the char amount, and nitrogen flow rate affects the bio-oil yield. Curvature was detected with char making linear regression unsuitable for modeling. Surprisingly, the nitrogen flow rate p-value for bio-oil quality was also less than 0.05 indicating that the bio-oil quality is also significantly affected by the nitrogen flow rate. Despite the low R^2 value for bio-oil quality, the p-value of nitrogen represents a mean change in response with nitrogen when the other factors are constant. This indicates that using H-NMR is a valid method for measuring bio-oil quality.

Generally, higher nitrogen flow is beneficial to limit the residence time of the gas and decrease the number of secondary reactions resulting in char. However, the high nitrogen flow also decreases the amount of residence time of the gases in the condensers. This causes a decrease in bio-oil yield due to inadequate condensing. A similar result with nitrogen flow rate decreasing bio-oil yield was also seen in the research conducted by Ersan Putun [15]. This indicates that the pyrolysis system could be improved by increasing the cooling rate of the condensers and ice bath. The increased nitrogen flow also causes a statistical significant decrease in bio-oil quality according to the data.

3.2. Catalyzed bio-oil results

Based upon the DOE, the catalyst tests were run with a nitrogen flow of 0.5 L/min, a reactor temperature of 500°C, and particle size between 2.8 mm and 5.0 mm. A maximum bio-oil yield at 500°C was observed by Ouarzki et al [16]. Additionally, due to the nitrogen flow results, downstream of the pyrolysis reactor was shortened to decrease residence time of the gas and decrease secondary reaction. This is expected to increase the yield of bio-oil.

The bio-oil from pyrolysis had an organic phase and an aqueous phase. The uncatalyzed oil from the design of experiment had only between 0-5% organic-phase, so the pyrolysis parameters were optimized by analyzing the aqueous-phase of the bio-oil. However, when a catalyst was used and the downstream was shortened, the organic-phase increased to ~12% of the total bio-oil. The yields are shown below in Figure 1. The gas yield was calculated by subtracting the measured mass of the char and bio-oil from the initial feed. The uncatalyzed bio-oil had the highest yield which decreased when catalysts were used. ZSM-5 and ZrO_2-TiO_2 decreased the bio-oil yield and increased gas yield signifying catalytic activity. A similar pattern in yields was seen with a similar comparison study by S.D. Stefanidis [9]. The aqueous-phase contains a large percent of water which can be harmful to GC-MS columns. Therefore, the aqueous-phase of the bio-oil was analyzed with H-NMR and the organic-phase was analyzed with GC-MS.

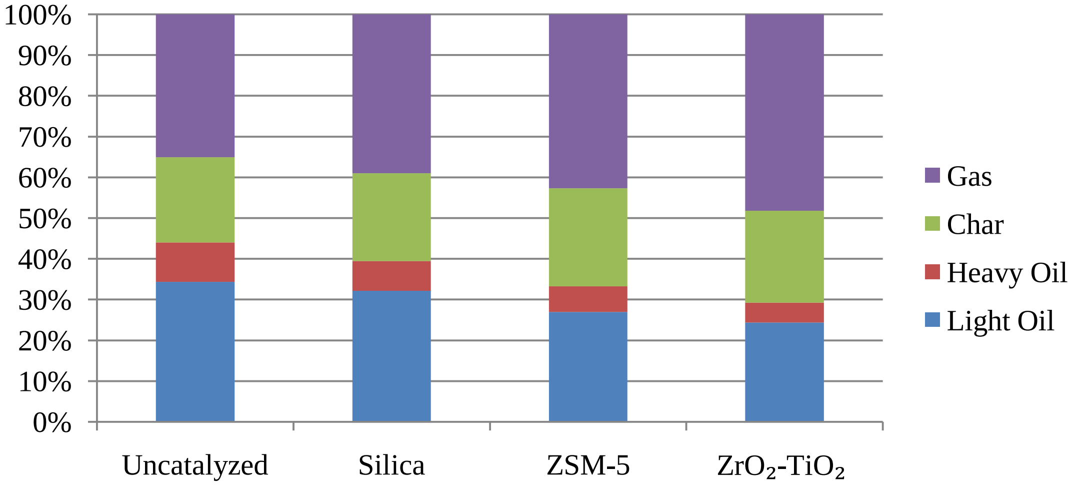

Figure 1: Gas, char and oil yields of pyrolysis process with catalyst

3.2.1. H-NMR results

The catalyzed bio-oil and uncatalyzed bio-oil aqueous-phase were analyzed with H-NMR to understand the overall hydrogen functional groups and compared them with commercial polyalphaolefin oil. The H-NMR spectra for the five bio-oils can be seen below in Figure 1.

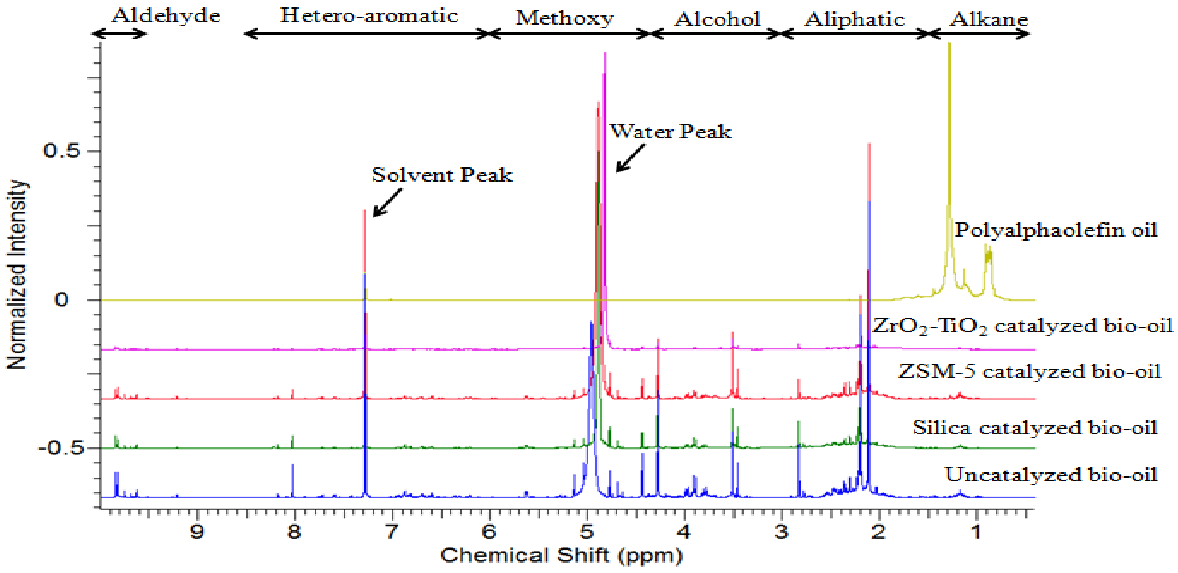

Figure 2: H-NMR results for bio-oil aqueous-phase

The labeled $CDCl_3$ solvent peak was used as a reference for the bio-oil samples. The polyalphaolefin sample appears to only have alkane and aliphatic groups while the bio-oil samples contain aldehydes, hetero-aromatics, methoxy, alcohols, aliphatics and alkanes. Comparing the bio-oil samples are visually difficult so integration was used. The water and solvent peak were removed before integration. The results of the integration can be seen below in Figure 2.

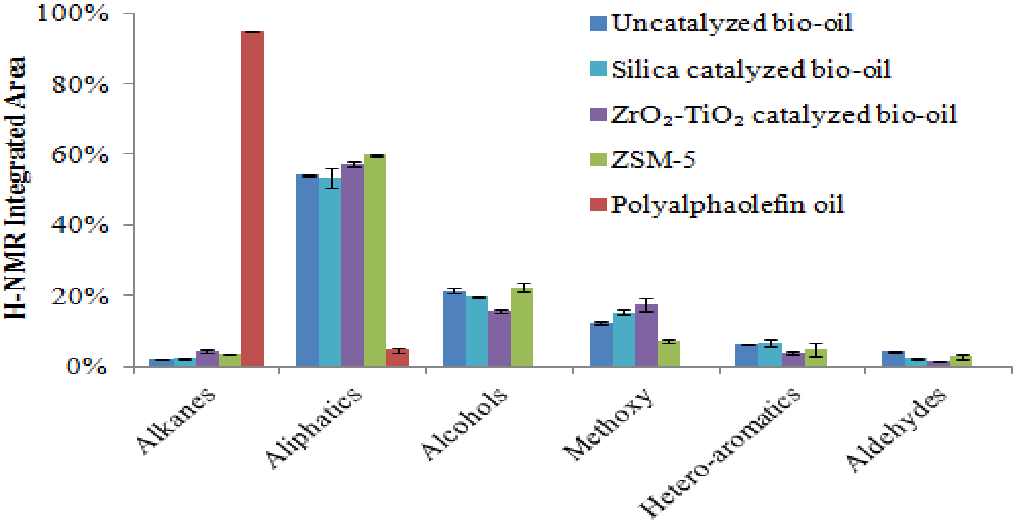

Figure 3: Integrated H-NMR results for bio-oil aqueous-phase analyzed in duplicate. Standard deviation is shown by the bracket

The ZrO_2-TiO_2 and ZSM-5 catalyzed bio-oil had a slightly increased alkane and aliphatic integrated region when compared to uncatalyzed bio-oil. Both catalysts decreased the concentration of aldehydes compared with uncatalyzed bio-oil. Both ZrO_2-TiO_2 and ZSM-5 improve the quality of the bio-oil aqueous-phase by increasing percent of aliphatic hydrogen.

The ZrO_2-TiO_2 was chosen because Qiang Lu and others showed that it increased the hydrocarbon content from 0.1% to 13.1% and was the best out of numerous catalysts tested when compared with uncatalyzed bio-oil [8]. In the results above, the alkane section is slightly increased and is the highest for the ZrO_2-TiO_2 catalyst. In order to compare the samples' bio-oil quality, the % alkane + aliphatic area from H-NMR was used. The results are shown below in Figure 3.

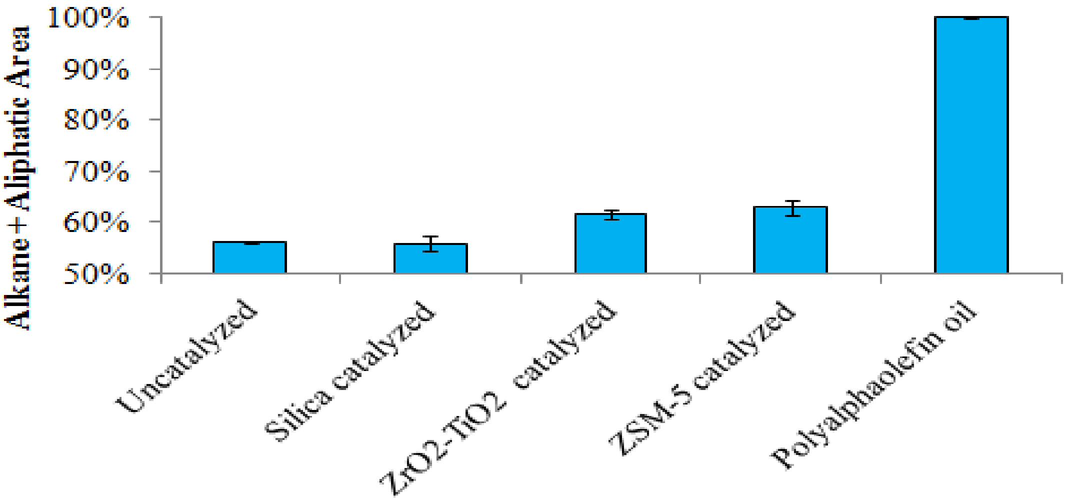

Figure 4: Bio-oil quality calculated with H-NMR. Each test was conducted in duplicate. Standard deviation is shown by the bracket.

The % alkane + aliphatic area from H-NMR is shown above in Figure 3 and is as follows; uncatalyzed (56%±0.2%), silica bead (56±1%), ZrO_2-TiO_2 (62±1%), and ZSM-5 (63±1%). The polyalphaolefin oil had a % alkane + aliphatic area of 100%. As the number of hydrogen atoms next to oxygen atoms decrease, the bio-oil quality will increase with this calculation method. While the purpose of this paper was to compare ZSM-5 and ZrO_2-TiO_2, the bio-oil quality for the two catalysts was nearly identical at 62% and 63% for the aqueous phase, which is within the standard deviation of the system. However, ZSM-5 had slightly increased alcohol and decreased methoxy when compared to ZrO_2-TiO_2. While H-NMR was able to quickly get an overview on the bio-oil quality of the aqueous phase, GC-MS was conducted on the organic phase of the bio-oil to get more detailed information on the composition and better understand the effect of the catalyst.

3.2.2. GC-MS results

The GC-MS results for the uncatalyzed, silica catalyzed, ZSM-5 catalyzed, and ZrO_2-TiO_2 catalyzed organic-phase bio-oil are below in Figure 5. Some peaks could not be identified due to fragmentations in the El-MS and only peaks with a match score over 80 were considered. The main peaks are labeled below in Figure 5.

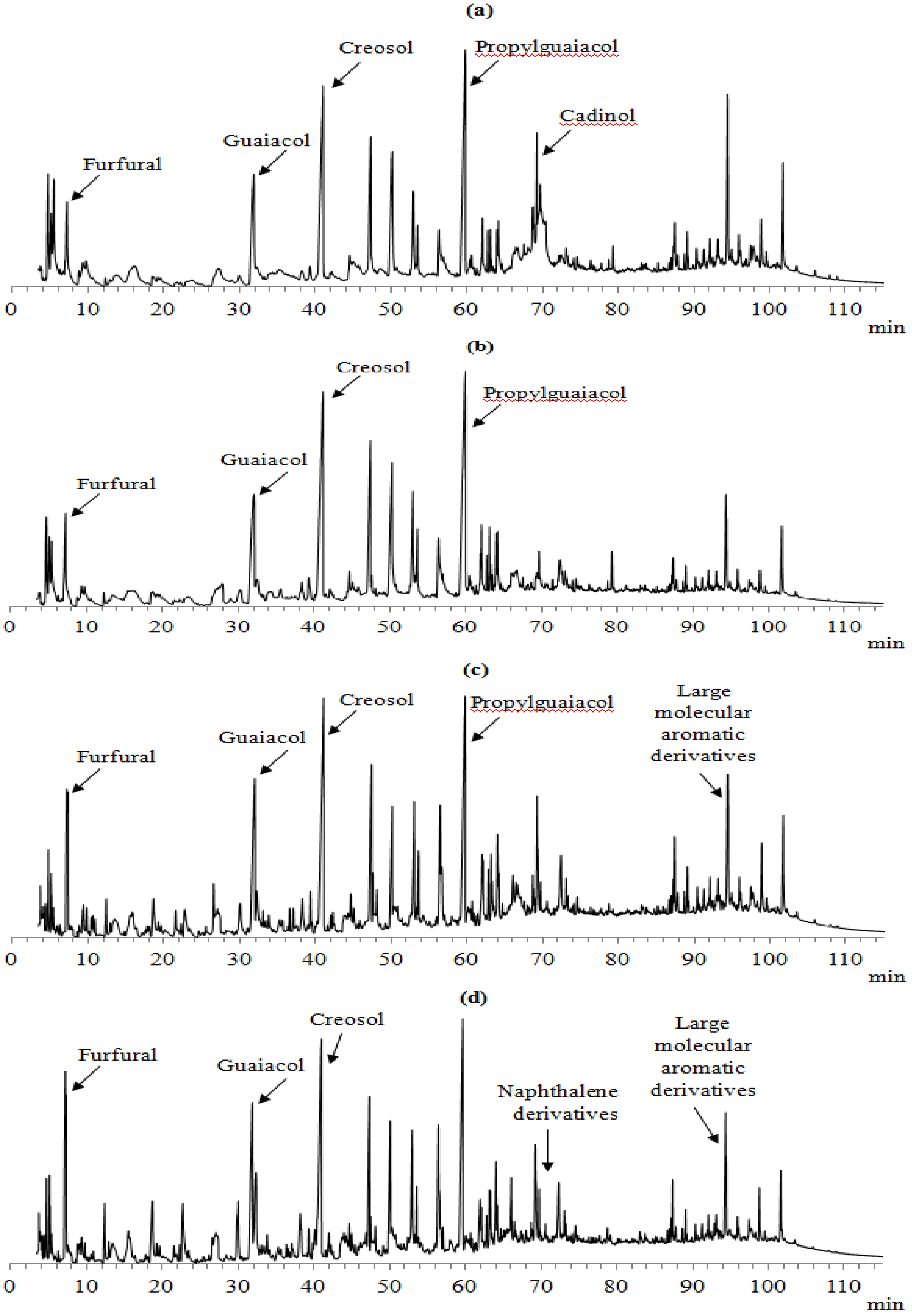

Figure 5: GC-MS of organic-phase bio-oil catalyzed with (a) Uncatalyzed; (b) Silica; (c) ZSM-5; (d) ZrO_2-TiO_2

The main products of pyrolysis are furfural, guaiacol, creosol, and propylguaiacol. The pyrolysis of Japanese cedar results in a large amount of phenolic compounds. The main difference between ZSM-5 and ZrO_2-TiO_2 catalyzed and non-catalyzed samples is the increase in the increase the number of compounds. The uncatalyzed and silica catalyzed bio-oil had 203 and 222 identified peaks while the ZrO_2-TiO_2 and ZSM-5 had 325 and 312 identified peaks.

The peaks from each spectrum were integrated, identified using the mass spectrum and classified. The peaks were classified according to 9 different groups: acids, aldehydes, alcohols, cyclopentanones (CP), furans, hydrocarbons (HC), ketones, phenols, and aromatics (AR) according to work done by others and shown below in Table 5 [8], [16].

Table 5: **Composition of organic-phase bio-oil products (peak area% of identified peaks)**

Catalyst	Acid	Aldehyde	Alcohol	CP	Furans	HC	Ketone	Phenols	AR	Others
None	3%	2%	4%	3%	9%	5%	6%	53%	8%	7%
Silica	2%	2%	0%	2%	8%	5%	4%	66%	11%	0%
ZrO_2-TiO_2	2%	1%	0%	10%	8%	4%	2%	60%	11%	1%
ZSM-5	2%	1%	2%	5%	10%	3%	2%	56%	17%	2%

As seen in Table 5, non-catalytic fast-pyrolysis bio-oil consists mostly of phenols (53%). The silica catalyst support made very little difference on the pyrolysis bio-oil products except for increasing phenols. The ZSM-5 catalyst doubled the amount of aromatics increasing them from 8% to 17% and also increased phenolic compounds. This trend is consistent with other researchers who also show that ZSM-5 catalyst increases aromatics[18], [19], [20]. The ZrO_2-TiO_2 catalyst also increased the aromatics to 11% from 8%. The main effect of the ZrO_2-TiO_2 catalyst was to increase the cyclopentanones from 3% to 10%, specifically forming 2-cyclopentenone at 5.6%. This is in good agreement with the results from Qiang Lu et al. who also observed an increase in cyclopentanones when using the ZrO_2-TiO_2 catalyst [8]. The ZrO_2-TiO_2 catalyst was also expected to increase the hydrocarbon content because Qiang Lu et al. saw an increase to 13.1%, but this was not observed with our results. This may be due to the slower pyrolysis experimental set-up used in this research. Both uncatalyzed and ZrO_2-TiO_2 catalyzed bio-oil had 4-5% hydrocarbon. However, the H-NMR did indicate a slight increase in alkane hydrogrens when ZrO_2-TiO_2 catalyst was used for the aqueous-phase of the bio-oil.

The difference in product distribution may be explained by the structure of the catalyst. The ZSM-5 has a pore size of 0.58 nm while the ZrO_2-TiO_2 has pore sizes of 11, 16, and 121 nm. Benzene has a size of 0.51 nm and may more effectively interact and react with the pore system and active sites of the ZSM-5 catalyst [21]. Additionally, aromatic yields were observed to be the highest with pore sizes in the range of 0.52 – 0.59 nm because the smaller pore size prevents the formation of larger catalytic products and catalytic coke due to size exclusion according to Jae, J. et al. [22]. Finally, ZSM-5 has been shown to convert cyclopentanones into benzene and napththalene products thereby decreasing cyclopentanones and increasing aromatics [23]. The ZrO_2-TiO_2 catalyst has larger pore sizes and lower surface area when compared to ZSM-5 and so the catalyst may be less active than ZSM-5 resulting in fewer aromatics. Overall, ZSM-5 is a better catalyst in both terms of bio-oil yield and bio-oil quality.

Conclusions

Central composite design determined that nitrogen flow significantly affected the pyrolysis bio-oil quality and quantity. Temperature significantly affected the char yield. Using the central composite design data, the pyrolysis parameters were optimized. Calculating a numerical bio-oil quality based off the % alkane + aliphatic area from H-NMR allows statistical analysis to be done and can detect trends that may have been difficult to originally detect. This was proven with calculating that the nitrogen significantly affected the bio-oil quality when doing the central composite design. This method is quick and correlates the number of hydrogens next to carbon vs. the number of hydrogens next to oxygen and other elements. H-NMR is a suitable analysis technique for quickly determining the overall bio-oil quality.

After the pyrolysis parameters were optimized, catalyst testing was conducted using ZrO_2-TiO_2, ZSM-5 and silica. The bio-oil aqueous-phase was first analyzed with H-NMR. The silica had minimal affect on the bio-oil quality however; ZrO_2-TiO_2 and ZSM-5 catalyst increased the bio-oil quality. ZSM-5 increased the % alkane + aliphatic area from 56% to 63% while the ZrO_2-TiO_2 increased the % alkane + aliphatic area from 56% to

62%. With direct comparison from H-NMR, no significant difference is seen between the two catalysts in terms of bio-oil quality. The ZrO_2-TiO_2 slightly increased the number of alkane hydrogens.

GC-MS was also conducted on the bio-oil organic-phase samples to get more insight into the compounds found within the bio-oil. It was found that ZSM-5 doubled the amount of aromatics from 8% to 17% and that ZrO_2-TiO_2 increased the amount of cyclopentanones from 3% to 10% as determined by GC-MS area %. ZrO_2-TiO_2 was also expected to increase the number of hydrocarbons, but a significant increase was not observed with our experimental pyrolysis set-up.

This work shows that H-NMR is a powerful tool for quick evaluation of bio-oil quality to optimize pyrolysis operating parameters. The effects of ZSM-5 catalyst and ZrO_2-TiO_2 catalyst were successfully analyzed using H-NMR and GC-MS. Further research is under progress which includes surface modifications to the ZrO_2-TiO_2 and silica catalyst. Additionally, regeneration studies will be conducted to reveal whether the catalysts are suitable for upgrading biomass fast pyrolysis vapors.

Acknowledgments- This research was supported in part by the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT) and by the Tokyo Institute of Technology Academy for Co-creative Education of Environment and Energy Science (ACEEES) program. The authors would like to thank the Kunio Yoshikawa lab in the transdisciplinary science and engineering department for use of the GC-MS equipment.

References

1. Höök M., Hirsch R., Aleklett K.., *Energy Policy,* 37 (2009) 2262.
2. Aleklett K, Cambell CJ., *Miner Energy.* 18 (2003) 5.
3. Acquaye A., Sherwen T., Genovese A., Kuylenstierna J., Koh L, McQueen-Mason S., *Renew. and Sustainable Energy Rev.* 16 (2012) 5414.
4. Lynd, L.R., Cushman, J.H., Nichols, R.J., Wyman, C.E. *Science.* 251 (1991) 1318.
5. Wang Y., He T., Liu K., Wu J., Fang Y., *Bioresour. Technol.* 108 (2012) 280.
6. Veses A., Puertolas B., Callen M, Garica T., *Microporous Mesoporous Mater.* (2015) 1.
7. Kelkar S., Saffron C., Andreassi K., Li Z., Murkute A., Miller D., Pinnavaia T., and Kriegel R., *Appl. Catal., B.* 174-175 (2015) 85.
8. Lu Q., Zhang Y., Tang Z., Li W., and Zhu X., *Fuel.* 89 (2010) 2096.
9. Stefanidis S., Kalogiannis K., Iliopoulou E., Lappas A., Pilavachi P., *Bioresource Technol.* 102 (2011) 8261.
10. Woodchip Garden. [Online] [Cited: 06 17, 2015.] http://moko.shop-pro.jp/.
11. Manya J., Ortigosa M., Laguarta S., Manso J., *Fuel.* 133 (2014) 163.
12.Gromping U., "Tutorial for designing experiments using the R package RcmdrPlugin.DoE, Report 4/2011, Reports in Mathematics, Physics and Chemistry." *Appl. Sci.* 2011.
13. Mullen C., Strahan G., and Boateng A., *Energy fuels.* 23 (2009) 2707.
14. ACD/Strcuture Elucidator, version 12.01, Advanced Chemistry Development, Inc., Toronoto, ON, Canada. [Online] 2015. www.acdlabs.com.
15. Ersan P., Energy. 35 (2010) 2761.
16. Ouarzki I., Hazi M., Luart D., Len C., Ould-Dris A., *J. Mater. Environ. Sci.* 7 (2016) 1008.
17. Fermoso J., Hernando H., Jana P., Moreno I., et al., *Catal. Today.* 277 (2016) 171.
18. Engtrakul C., Mukarakate C., Starace A., Magrini K., Rogers A., and Yung M., *Catal. Today.* 269 (2016) 175.
19. Foster A., Jae J., Cheng Y., Huber G., Lobo R., *Appl. Catal., A.* 423-424 (2012) 154.
20. Du Z., Ma X., Li Y., Chen P., Liu Y., Lin X., Lei H., Ruan R., *Bioresour. Technol.* 139 (2013) 397.
21. Mihalcik D., Mullen C., Boateng A., *J. Anal. Appl. Pyrolysis.* 92 (2011) 224.
22. Jae J., Tompsett G., Foster A., Hammond K., et al., *J. Catal.* 279 (2011) 257.
23. Horne P., and Williams P., *Renew. Energy.* 7 (1996) 131.

(2017) ; http://www.jmaterenvironsci.com