

Catalytic Fast Pyrolysis of Cassava Rhizome in a Micro-Reactor

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Abstract: Cassava rhizome was subjected to catalytic pyrolysis at 500°C using analytical pyrolysis method, coupled with gas chromatography/mass spectrometry technique (Py-GC/MS). The relative effects of various catalysts on the pyrolysis products were investigated. The catalysts applied were zeolites types (ZSM-5, Al-MCM-41 and Al-MSU-F), metal oxides (Zinc oxide, Zirconium (IV) oxide, Cerium (IV) oxide and Copper Chromite catalysts), proprietary commercial catalysts (Criterion-534 and Alumina-stabilised Ceria-MI-575) and natural catalysts (slate, char and ash). The chromatographic peak areas of the pyrolysis products were analysed, using principal component analysis (PCA). Results showed that the zeolites, proprietary commercial catalysts and copper chromite were found to be selective to the reduction of most oxygenated lignin derivatives, indicating an improvement of bio-oil viscosity. The use of ZSM-5, Criterion-534 and Al-MSU-F catalysts were found to enhance the

formation of aromatic hydrocarbons and phenols, which are valuable products for fuel and chemical industries. In addition, we can predict that the studied catalysts, except MI-575, would increase the bio-oil products acidity provided that the water level remains the same.

Keywords: Cassava rhizome, Pyrolysis, Catalysts, GC/MS, Principal component analysis, Bio-oil.

1. INTRODUCTION

Biomass, a type of renewable sources, exists in large amounts and is readily available for energy production in many developing countries. Using thermochemical processing, such as fast pyrolysis, biomass can be transformed into liquid bio-oil, which can be stored and used for different applications. The main properties and applications of bio-oil were recently reviewed by Czernik and Bridgwater [1]. Bio-oil is known to be viscous, acidic, and thermally unstable, and contains high proportion of oxygenated compounds. The challenge is to produce bio-oil of high quality that can replace or supplement current fossil fuel usage. One way to ensure this is to improve the quality of bio-oil produced either at source prior to full production or by upgrading the product. One of the possible upgrading options for improving bio-oil quality is the addition of catalysts into the pyrolysis process.

The intended purposes of using catalysts are to (i) enhance the cracking reactions of the heavy molecules in pyrolysis products leading to the production of less viscous bio-oil, (ii) reduce the

formation of carboxylic acids making bio-oil less corrosive and (iii) enhance the formation of more valuable products, like hydrocarbons, that can increase the heating value of the bio-oil.

The rhizome of cassava plants was selected as the feedstock in this study. Cassava (*Manihot esculenta* Crantz) is a shrubby perennial crop and is harvested approximately 12 months after planting. At harvest time, the top parts of the plants are cut before being uprooted. After the tubers are taken off as the main product, the rhizome is usually left in the field as compost. In Thailand, for example, more than 14 million tonnes of cassava rhizome is produced annually with potential use for energy production.

2. METHODOLOGY

2.1 Biomass

Cassava rhizome (CR) from Nakhon Ratchasima province in Thailand was used as feedstock in this study. The rhizome was ground to particle size less than 100 μm and its main characteristics are shown in Table 1.

2.2 Catalyst

Selected catalyst samples were used to investigate the impact on pyrolysis product distribution and subsequently to predict the change in bio-oil properties. Table 2 shows the representative catalyst samples and their main properties.

Table 1. Proximate, ultimate and component analyses of biomass samples.

Proximate Analysis		Ultimate Analysis		Component Analysis	
Component	wt% ^a	Element	wt% ^b	Component	wt% ^c
Volatile matter	71.29	C	51.59	Cellulose	27.82
Fixed carbon	16.69	H	6.69	Hemicellulose	39.67
Ash	3.71	N	1.27	Lignin	21.71
Moisture	8.31	O	40.45	Extractives ^d	10.80
		S	< 0.10		

^a As-received basis^b Dry, ash-free basis^c Dry basis^d 95% Ethanol/toluene (1/2, by volume), followed by 95% ethanol and hot water**Table 2.** Characteristics of selected catalyst samples.

Catalyst types	Name	Source	Composition	Surface area (m ² /g)
Zeolites*	Zeolite ZSM-5 type	BDH (UK) Company	Si/Al ratio: 50	300
	Aluminosilicate mesostructured, hexagonal framework, Al-MCM-41 type	Sigma-Aldrich Company Ltd.	Si/Al ratio: 40	1120
Metal oxides	Zinc oxide	Acros Organics	99.5% ZnO	77
	Cerium (IV) oxide	Acros Organics	99.9% CeO ₂	144
Proprietary commercial catalysts	Alumina Stabilised Ceria (MI-575)	GRACE Davison	71.0% CeO ₂ , 25.0% ZrO ₂ , 2.2% La ₂ O ₃ , 0.10% Al ₂ O ₃ and 0.1% CaO	55
Natural catalysts	Slate calcined at 750 °C	Thailand	Mainly SiO ₂	164

*The mean pore diameters of zeolites ZSM-5 and MCM-41 are 5.5 and 31 Å, respectively.

2.3 Pyrolysis GC/MS

Pyrolysis experiments were carried out, using a pyrolysis autosampler CDS AS-2500 with pyroprobe CDS 2000. Approximately 0.5 mg of cassava rhizome was placed in a quartz tube along with a quartz filler rod. In catalytic pyrolysis experiments, the catalyst was placed above the biomass as a fixed bed and quartz wool was used to separate the biomass and catalyst layers. The amount of catalysts was 0.5 mg (to obtain 1:1 biomass: catalyst ratio). The pyroprobe programme was at 500°C for 0.01 second at the heating rate of 3000°C/second and was held for 10 seconds.

PerkinElmer AutoSystem XL Gas Chromatograph was used to separate the pyrolysis vapours. The column used was PP 1701 60m x 25 μm with a 0.025 μm film thickness. Helium at a velocity of 38 cm/s was used as a carrier gas and the split injection ration was 1:125. In addition, the oven programme started at 45°C for 4 minutes and then was heated at a heating rate of 4°C/min to 240°C. The injector and detector temperature was set at 280°C.

The separated compounds were then analysed using a PerkinElmer Turbomass Gold Mass Spectrometer in Electron Impact (EI) mode. The mass spectra were obtained at the ionisation energy of 70 eV from m/z 28 to 600 with the speed of 1.0 second/decade.

Identification of chromatographic peaks from pyrolysis GC/MS experiments was carried out by comparing the mass ions (m/z) of each peak with NIST mass spectral database and literature data of pyrolysis products from lignocellulosic materials [2-3]. Four experimental

runs were performed per sample and the averaged values were used for analysis.

2.4 Principal component analysis (PCA)

The Unscrambler software was used in this study for calculating principal components and generating score and loading plots. The score and loading plots are the maps of samples and variables, respectively. The principal component analysis has been used previously in analytical pyrolysis and found to be useful technique for the complex data [4]. The PCA theory and interpretation can be found in chemometrics or statistics literature [5].

3. RESULTS AND DISCUSSION

In this study, cassava rhizome samples were pyrolysed in a fixed-bed micro-reactor at 500°C. The pyrolysis vapour produced was then passed through a fixed-bed of catalyst to undergo catalytic reactions. The catalytic pyrolysis vapour including bio-oil range compounds and non-condensable gases was passed into a GC column and subsequently the separated compounds were analysed, using mass spectroscope (MS). Since bio-oil range products were not condensed in this reactor setup, it is not possible to quantify the bio-oil yields. Nevertheless, the relative amount of each chemical in bio-oil in terms of the percentage of the chromatographic peak areas was used in the analysis of catalytic effects on bio-oil quality.

The chromatograms obtained, with and without zeolite catalysts, are presented in Fig. 1. Table 3 lists 34 main chromatographic peaks

identified in order of their retention times. Fig.1 is an example of the typical chromatograms acquired from Py-GC/MS. This example shows how difficult it is to visually observe and predict the effect of catalysts on pyrolysis products. Therefore, the averaged percentages of peak areas from the chromatograms were subjected to statistical analysis, using the principal component analysis (PCA) method.

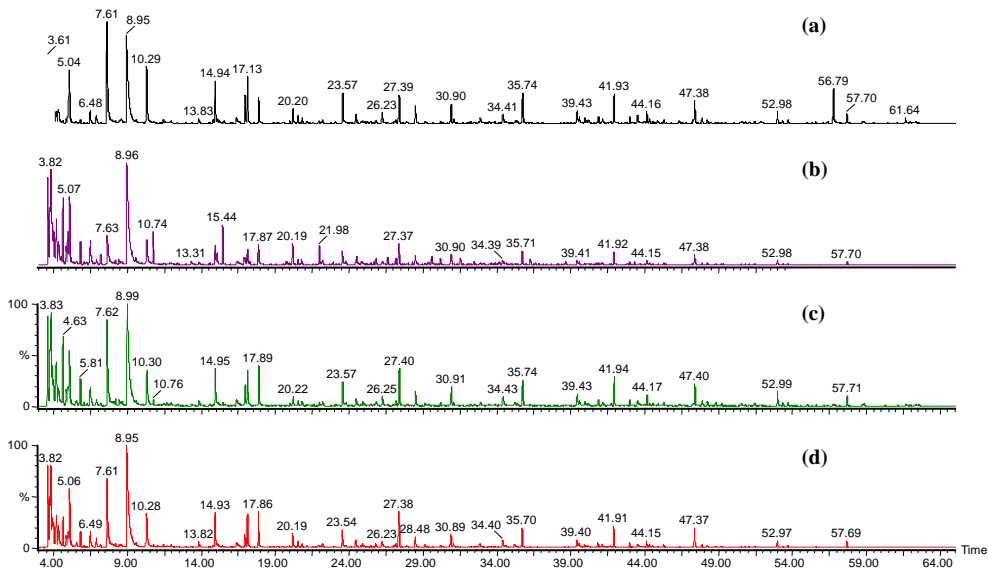


Figure 1. Chromatograms of cassava rhizome pyrolysis products (a) without catalyst, (b) with ZSM-5, (c) with Al-MCM-41 and (d) with Al-MSU-F type.

PCA is known to be useful tool for interpretation of multivariate or complex data. Its score plot is used to observe the interrelationships of samples, or catalysts in this case, whereas the loading plot shows the interrelationships of variables, or pyrolysis products in this case. To study the relationship between catalysts and pyrolysis products, the

score and its corresponding loading plot must be considered together.

Table 3. Chromatographic peak identification of cassava rhizome pyrolysis products.

Peak ID	R/T (min)	Compound name	Origin*	Peak ID	R/T (min)	Compound name	Origin*
1	4.17	Acetaldehyde	C	18	23.57	2-Hydroxy-2-cyclopenten-1-one	C
2	4.28	Methanol	C	19	26.23	2(5H)-Furanone	C
3	4.60	Furan	C	20	26.62	p-Ethyl-styrene	L
4	5.07	1,2-Propanedione	C	21	29.59	5-Methylindan	L
5	6.48	2,3 Butanedione	C	22	30.19	Phenol	L
6	7.19	Benzene	L	23	30.90	Guaiacol	L
7	7.61	Hydroxyacetaldehyde	C	24	31.51	4,7-Dimethylindan	L
8	8.61	Lactic acid	C	25	32.46	2-Methyl phenol	L
9	8.95	Acetic acid	C	26	35.74	4-Methylguaiacol	L
10	10.29	1-Hydroxy-2-propanone	C	27	39.43	4-Ethyl guaiacol	L
11	10.74	Toluene	L	28	41.93	4-Vinylguaiacol	L
12	13.82	2-Propenoic acid, methyl ester	C	29	44.16	Syringol	L
13	14.94	3-Hydroxypropanal	C	30	47.38	Trans-Isoeugenol	L
14	16.89	m-Xylene	L	31	52.98	4-Vinyl syringol	L
15	17.13	2-Hydroxy-3-oxobutanal	C	32	56.79	Levoglucosan	C
16	17.87	Furfural	C	33	57.70	4-Propenyl syringol (trans)	L
17	20.20	2-Furfuryl alcohol	C	34	61.64	trans-Coniferyl alcohol	L

*The letters C and L represent carbohydrate and lignin, respectively.

It is important to note that the axes of the score and loading plots are calculated based on the maximization of the variance of the input data, which are the percentages of the chromatographic peak areas in this case. The first and most important axis that lies along the direction of maximum variance in the data set is called the first principal component, denoted as PC1, whereas the second and the

third are PC2 and PC3. Each principal component explains different amounts of information, which can be noticed from the percentage value at the bottom of the PCA plots. The high percentage value of the PC means that the amounts of the information that can be explained by that particular PC is also high.

The key point for the interpretation of the PCA plots is that if the samples or variables are clustered or stay in the same location of the plots, they exhibit similar behavior. If the sample(s) in the score plot located in the same position as variable(s) in the loading plot, the sample(s) have statistically high value of the variable(s). Conversely, if the sample(s) lie in the opposite direction to the variable(s), sample(s) have statistically low value of the variable(s).

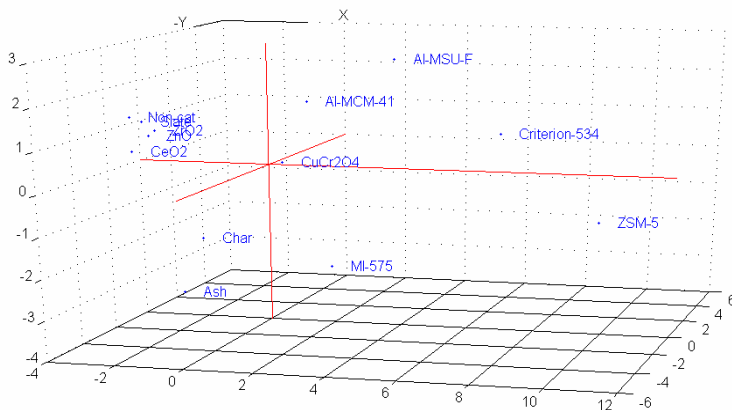
The first PCA model was established with all catalyst samples used and all compounds in order to view the distribution of catalysts and compounds through the score and loading plots. Fig. 2 presents the score (a) and its corresponding loading plots (b) for the first three principal components, PC1, PC2 and PC3, representing 57%, 18%, and 9% of the total variance, respectively. This means that up to 84% of the data can be explained by these figures, while the residual variance (16%) may be regarded as noise in data. It is apparent from the score plot of Fig.2 that there is a cluster of samples on the negative side of PC1 (X-axis). This cluster, including “CeO₂”, “ZnO”, “ZrO₂”, “Slate” and “Non-cat”, indicates similar behaviour on pyrolysis product distribution. Since the “Non-cat” in the plot is the controlled sample without any catalyst, it is logical to conclude that CeO₂, ZnO, ZrO₂ and Slate are not active enough under the conditions studied to

change the pyrolysis products or bio-oil quality. Consequently, those catalysts are excluded for the next PCA model.

Viscosity is one of the most important properties of bio-oil, especially if its application involves pumping and injecting. It is known that the viscosity of bio-oil has a positive correlation with its molecular weight [6] and most of the heavy pyrolysis products are derived from lignin. Therefore, the second PCA model included all lignin-derived compounds and the selected catalysts. Its score and corresponding loading plots are presented in Fig 3. It is expected from this model that catalysts that help to reduce the lignin derivatives would have the potential for decreasing the bio-oils' viscosity.

Fig. 3 reveals that there are two main groups of compounds separated by the first principal component which explains up to 66% of the total variance. One is on the negative PC1, which contains mainly oxygenated lignin derivatives and the other one is on the positive PC1, which is composed of aromatic hydrocarbons (IDs 20, 21, 24, 6, 11 and 14) and phenols (IDs 22 and 25). When looking at the score and the corresponding loading plot together to observe the relationship between catalysts and pyrolysis products, it is evident that ZSM-5 zeolite dominating the positive PC1 shows a high potential not only for reducing the oxygenated lignin compounds, which is advantageous to bio-oil viscosity improvement, but also for enhancing the production of aromatic hydrocarbons and phenols, which are valuable products for fuel and chemical industries. In addition, the Criterion-534 and Al-MSU-F catalysts also demonstrate similar behavior to the ZSM-5, although the effect is less pronounced on the PC1.

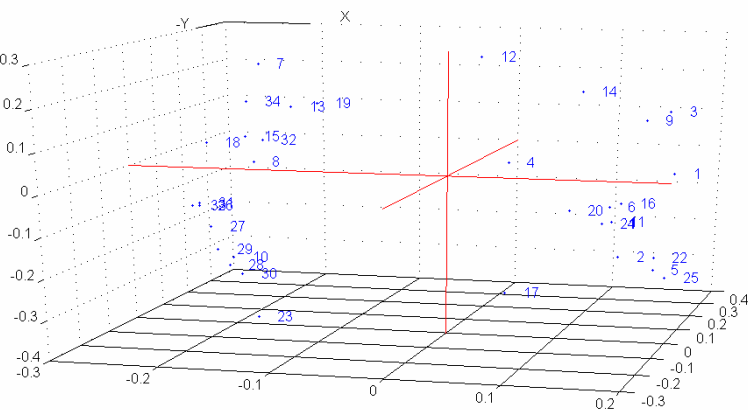
Scores



All, X-expl: 57%,18%,9%

(a)

X-loadings



All, X-expl: 57%,18%,9%

(b)

Figure 2. Score (a) and loading (b) plots of the first three principal components for the model with all catalysts and all compounds.

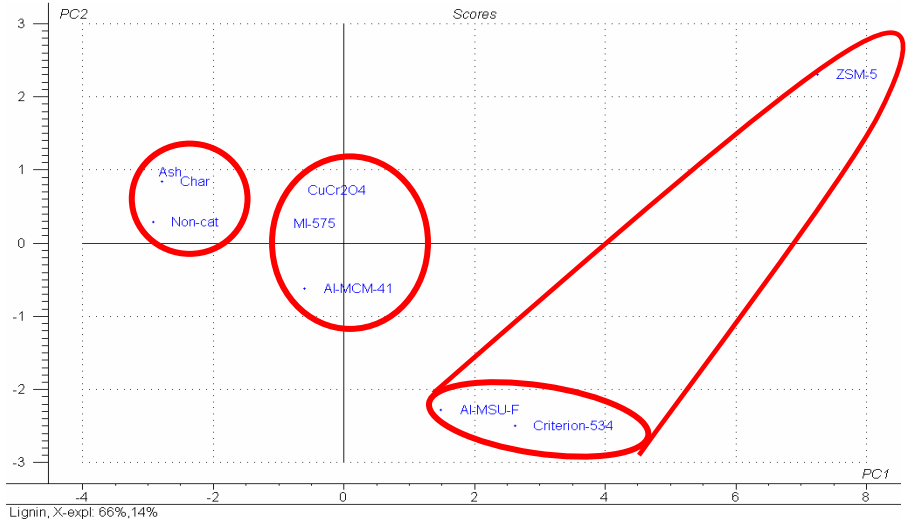
Another group of catalysts, lying near the origin of the score plot, are Al-MCM-41, MI-575 and copper chromite. They also show a slight improvement on decreasing oxygenated lignin compounds. This is because its position is away from the “Non-cat” sample and from the oxygenated lignin derivatives that lie on the negative PC1.

For catalysts containing alkali metals like char and ash, it seems that they do not show any tendency towards bio-oil quality improvement. Instead, they were found to slightly promote the formation of oxygenated lignin compounds, see Fig. 3. This can be an adverse effect on bio-oil quality. Therefore, it is suggested that in any pyrolysis reactor, char accumulation should be minimized and ash removal from biomass feedstock, for example, by washing should be performed prior to the pyrolysis processing.

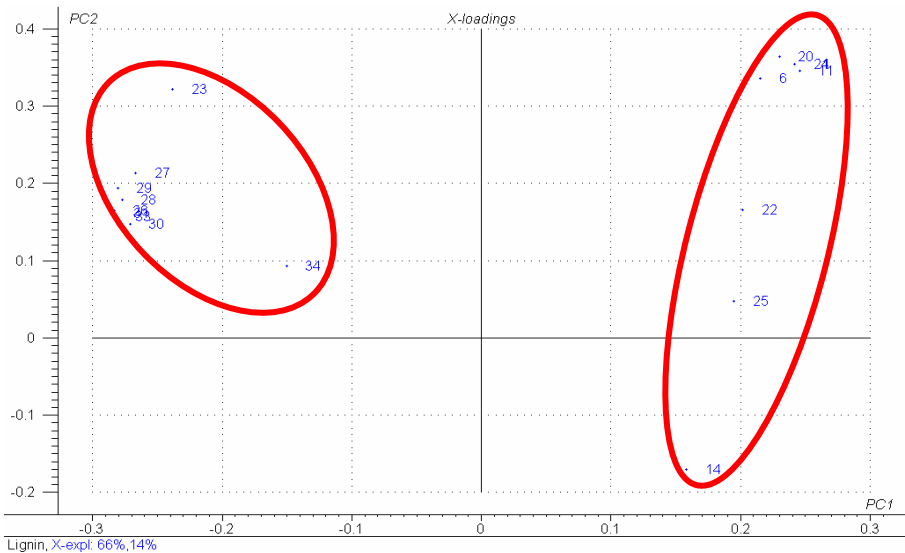
Aldehydes and ketones in bio-oil are thought to be responsible for many reactions that cause instability. Hence, to monitor the influence of catalysis on bio-oil stability, another PCA model was created. This model includes the active catalysts and all carbonyl compounds. The resultant score and loading plots are displayed in Fig. 4. It can be seen from these figures that all the catalysts alter the distribution of the carbonyl compounds because they lie away from the “Non-cat” sample in the score plot. Nevertheless, no single catalyst could reduce all of the carbonyl compounds. While the catalysts decrease the amounts of the carbonyls on the left side of the origin (negative PC1), they also increase the amounts of the carbonyls on the right side of the origin. Although the number of compounds on the negative PC1 is higher than that on the positive PC1, it is not

logical to conclude that catalysis will help to improve the bio-oil stability since it is not well understood that which compounds are more reactive. Therefore, fundamental research on reactivity of carbonyl compounds present in bio-oil is suggested for future study.

It is also imperative to monitor the carboxylic acid yields as they are responsible for the low pH value of bio-oils which causes corrosion problems in piping and fuel lines and in combustion engines. Two organic acids identified are acetic and lactic acids. Fig.5 compares their yields from different catalysts. It is obvious that most catalysts promote the formation of acetic acid, especially ZSM-5 and Al-MSU-F zeolites. Nonetheless, the MI-575 and ash catalysts do not seem to change the acetic acid yield significantly. The lactic acid is reduced in quantity by most catalysts, except for the ash, and it is even completely eliminated by Criterion-534 and MI-575 proprietary commercial catalysts. Acetic acid is known to be present in bio-oil in a much greater amount than lactic acid and its influence on bio-oil acidity is therefore much higher. Consequently, the effect of the acetic acid would outweigh that of the lactic acid, suggesting that all the catalysts lead to an overall increase in bio-oil acidity.

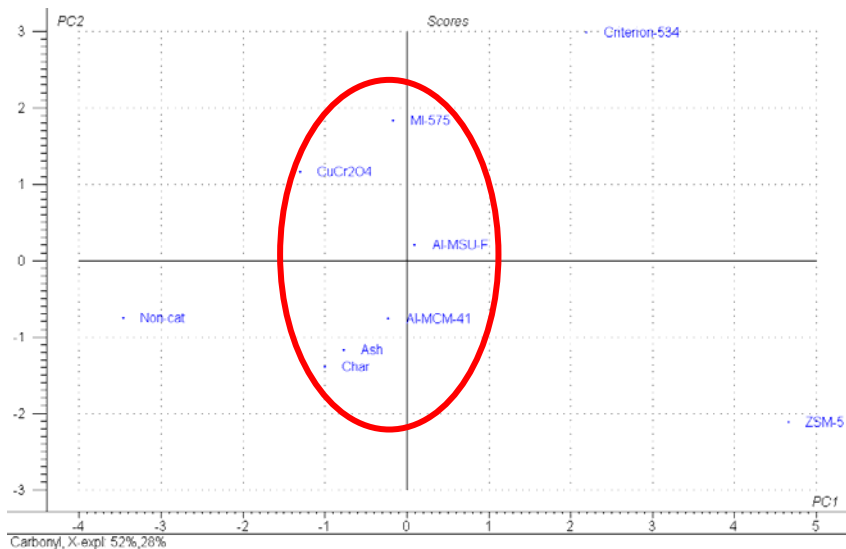


(a)

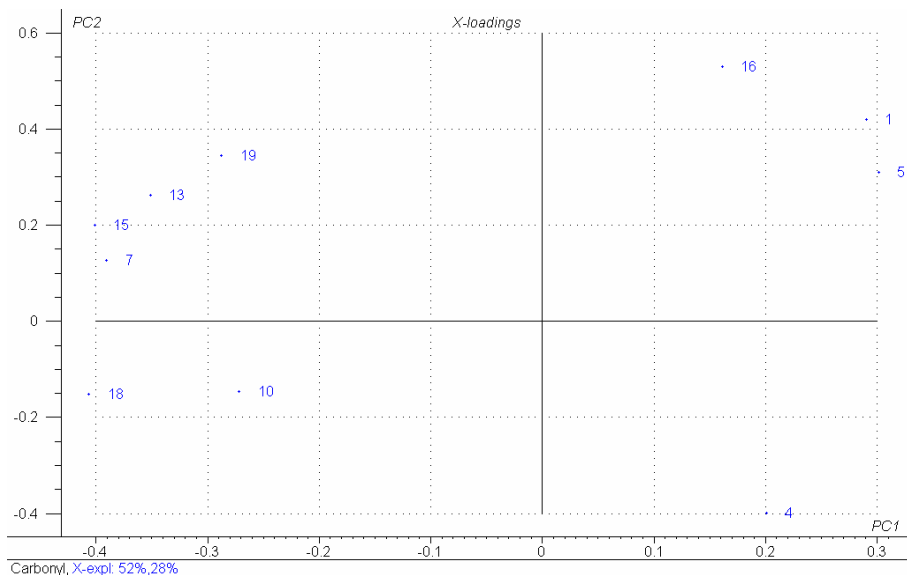


(b)

Figure 3. Score (a) and loading (b) plots of the first two principal components (PC1 and PC2) for lignin model.

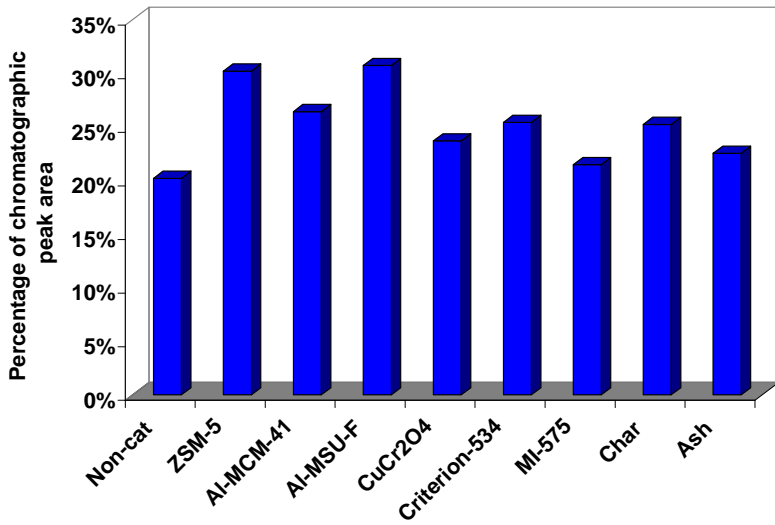


(a)

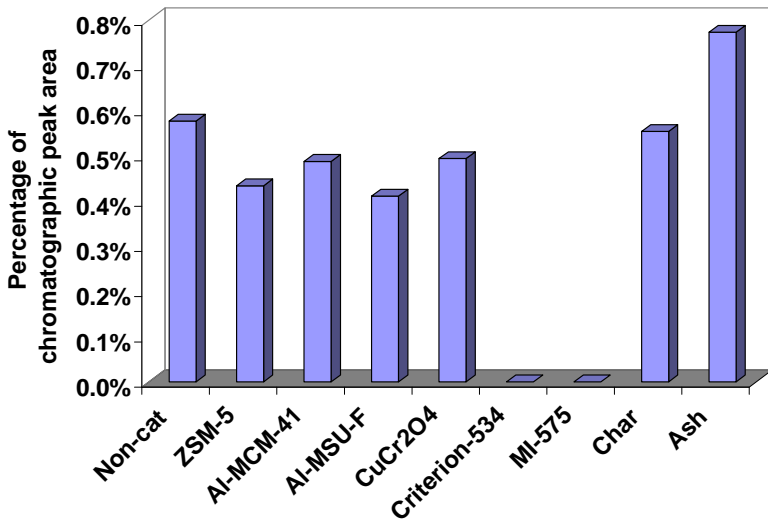


(b)

Figure 4. Score (a) and loading (b) plots of the first two principal components (PC1 and PC2) for carbonyl model



(a)



(b)

Figure 5. Comparison of acetic acid (a) and lactic acid (b) yields.

4. CONCLUSION

Various catalysts and chemicals were tested for their activity in changing biomass pyrolysis products. Catalysts, such as ZnO, ZrO₂, CeO₂, and slate, were found to be inactive under the condition studied. The ZSM-5 zeolite appears to be the most active catalyst as it increases the production of aromatic hydrocarbons and phenols, reduces most of the oxygenated lignin-derived compounds and produces a significant amount of acetic acid. The production of hydrocarbons and the reduction of oxygenated lignin species would result in an increase in bio-oil heating values and a decrease in bio-oil initial viscosity. The increase of the acetic acid yield seems to reduce the bio-oil fuel quality. However, this problem can be minimized or eliminated if the catalytic bio-oil is produced in a biorefinery plant where separation of acetic acid, phenols and other chemicals can be achieved. The other two catalysts that demonstrated similar catalytic behaviour to ZSM-5 zeolite on pyrolysis product distribution are Criterion-534 and Al-MSU-F, although the observed effect is less pronounced. In addition, the use of copper chromite, MI-575 and Al-MCM-41 catalysts demonstrate also the potential for improving the bio-oil viscosity.

5. ACKNOWLEDGMENTS

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6. REFERENCES

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