Ni$_2$Fe$_3$ Metal Catalyst and Cellulose Ratio Impact on Pyrolyzed Bio-Oil

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Abstract Carbon neutral bio-oil is needed to replace liquid fossil fuels in order to reduce CO$_2$ emissions and global warming. However, the quality of bio-oil produced from biomass contains too much sugar, which is undesirable. Investigating a new method to reduce sugar concentration by changing the ratio between cellulose and catalyst is necessary because other methods all require additional costs. In this study, the Ni$_2$Fe$_3$ and cellulose have been chosen as the model catalyst and model biomass compound, respectively. Five different ratios have been chosen for investigation, 4:1, 2:1, 1:1, 1:2 and 1:4 (weight ratio= cellulose: catalyst) The cellulose pyrolysis experiments results show the bio-oil yield increases as the catalyst amount or ratio is increased initially and then decreased. The 2:1, 1:1, 1:2 shows the highest yields among the five different ratios. From GC-MS analysis, the sugar reduction increases initially and then decreases. Based on both results, the best cellulose/catalyst ratio was 2:1 or 1:1, which is attributed to optimized heat conduction.

1. Introduction

Renewable liquid fuels are needed in order to reduce CO$_2$ emissions and global warming. The production of bio-oil as a transportation fuel is a potential answer (Muis *et al*., 2010; Krajačić *et al*., 2011; Shafiei and Salim, 2014; Charfeddine and Kahia, 2019). Bio-oil is produced through contemporary biological processes, typically involving renewable feedstocks such as biomass and possibly by anaerobic digestion. Bio-oil can also be derived directly from domestic resources, industrial and commercial waste.

Bio-oil produced through pyrolysis of biomass has a high oxygen content (e.g., sugars), low energy density, and it is hard to use for vehicles directly. Until now, various methods and techniques were used to remove sugar in order to reduce oxygen content. For example, pretreat the reactant before the experiment, Like Torr's group (Xin *et al*., 2019) used pretreatment pine wood to do the pyrolysis experiment, put the wood in 1 wt% acetic acid solution for 4 h. The result shows that this method could remove more than 10% sugar. Pressure distillation is also a useful method to remove sugar, reducing oxygen content. For example, reduced pressure distillation was performed to obtain distilled bio-oil by Zheng's group (Zheng and Wei, 2011). Through this method, they reduce the sugar content from 0.9% to 0.1%. Besides, some groups used supercritical solvents to remove oxygen, like Savage's group (Duan and Savage, 2011) that upgraded the crude algal bio-oil using supercritical water method (SCW). The SCW method can improve product oil by reducing sugar and oxygen content. However, there are few works focusing on finding how the ratio between biomass model compounds and catalyst influence the component of bio-oil. There is a clear need to choose a suitable catalyst and biomass in order to investigate this relationship. Based on our knowledge, an easy to recover and recycle homogenous cluster catalysts is the best choice to produce bio-oil efficiently.

A cluster is an ensemble of bound atoms or molecules that are intermediate in size between a molecule and a bulk solid. The metal cluster can also be used as a catalyst (such as Ru$_3$(CO)$_{12}$, Au cluster, etc.); they sometimes also bound to some other metal or cluster (Oguri *et al*., 2013). The cluster catalyst has excellent properties, the absence of large bulk phases leads to a high surface-to-volume ratio, which is advantageous in any catalyst application as this maximizes the reaction rate per unit amount of catalyst material, which also minimizes cost.

Considering potential large-scale applications, catalysts made of cheap and earth-abundant elements are crucial for economically viable energy conversion processes. Instead of using rare earth or expensive metals, it is better to focus on making catalysts with nickel and iron in order to build a new type of catalytic-cluster.

In this study, cellulose was chosen as the reactant for pyrolysis, because it is the major component of biomass and often used as a model compound. Then, the Ni$_2$Fe$_3$ cluster catalyst will be chosen as the catalyst

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model (based on our group's previous result). Five different ratios between cellulose and catalyst have been chosen to investigate the relationship between the cellulose/catalyst ratio and bio-oil component. The ratios are 4:1, 2:1, 1:1, 1:2 and 1:4. The final goal of this study is to discern how the ratio influences bio-oil composition in order to assess its economic feasibility.
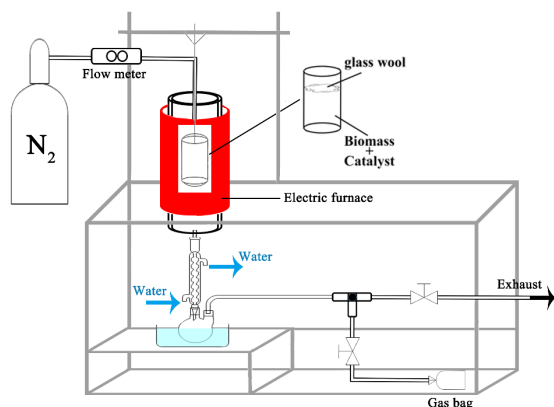
2. Experimental Method

2.1 Catalyst preparation

The biomass feed, 38 μm powdered cellulose from Wako Pure Chemical Industries, and cellulose was directly used without any modification.

The Ni_2Fe_3 catalyst is prepared by the sol-gel method, which method is appropriate to get cluster structural (De *et al*.,1996; Jayaprakash *et al*., 2015). The chemicals were citric acid, $Fe(NO_3)_3 \cdot 9H_2O$, ethylene glycol, and $Ni(NO_3)_2 \cdot 6H_2O$, as also purchased from Wako Pure Chemical Industries. The mol ratio between Metal ion (Ni, Fe) and citric acid is 1:1.2. The preparation of catalysts was performed at room temperatures following: 5.81 g $Fe(NO_3)_3 \cdot 9H_2O$ and 12.1 g $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 30 ml of distilled water and stirred for 5 hours. Then 5 ml of ethylene glycol and 11.1 g citric acid was added in a beaker. Then the transparent solution was stirred for 15 hours at which time the solution became uniform. The transparent sol was dried at 110^0C in an oven for 20 hours. Then using a furnace and calcined at 700^0C to burn off hydrocarbons under 95% N_2 and 5% H_2 mix gas. Finally, the catalysts were crushed into powder in a mortar and pestle. After repeating this process many times, enough catalyst was obtained.

2.2 Pyrolysis method

Cellulose (4 g) was loaded in a 50 mm diameter quartz reactor with a different mass of catalyst (1 g, 2g, 4g, 8g, 16g, respectively). Then the entire system was purged with flowing nitrogen gas for 7 min in order to expel all air. Afterward, the reactor was heated to the set temperature (450°C) with a heating rate of 45°C/min. Then the nitrogen gas carried the pyrolyzed vapors from the reactor to the condenser. The vapors were condensed using cold water by the condenser. The bio-oil was collected and analyzed by GC-MS. The amount of bio-oil and char and coke were weighed, and then the amount of gas was calculated by subtracting the amount of bio-oil and char & coke from the initial feed (Figure 1).

2.3 XRD and SEM test

XRD analysis of catalysts was conducted by X-ray Diffractometer (Mini Flex 600). 45 kV and 15 mA were used for the X-ray tube operation. The scan range (2 theta) of the XRD pattern was collected from 5° to 90° using filtered Cu radiation.

Images of catalysts were obtained by a scanning electron microscope (VE-9800) operated at 10 kV. The catalyst was firstly immersed in alcohol. Then the samples were loaded and dried on a copper grid (carbon-coated) before the test.

2.4 GC-MS analysis method

In order to identify organic compounds and analyze the component of the bio-oil samples, GC–MS equipment was used to analyze bio-oil samples. The analysis was performed on a GC-2010 Plus equipped with a GC–MS-QP2010 SE mass-detector made by Shimadzu. The column type was Stabilwax-DA 30 m x 0.25 mm, 0.25 μm diameter. The analysis was run with a 10 : 1 split entry. The oven temperature was held at 40°C for 5 min and then ramped to 50°C at 1°C/min. Next, it was ramped to 130°C at 2°C/min. Finally, the temperature was ramped to 260°C at 4°C/min and held for 10 min. The compounds were identified by comparing the mass spectra to NIST 11 MS library of compounds using the GC–MS software. A similarity threshold of over 80 was used to identify the compounds. All GC–MS experiments were conducted in duplicates, and the standard deviations were calculated.

Figure 1. Experimental set-up for pyrolysis experiment
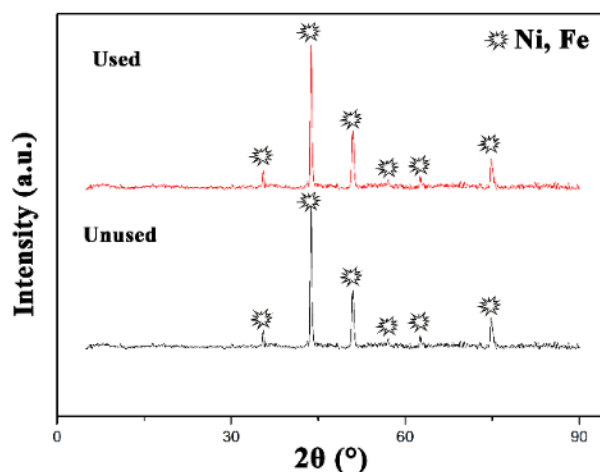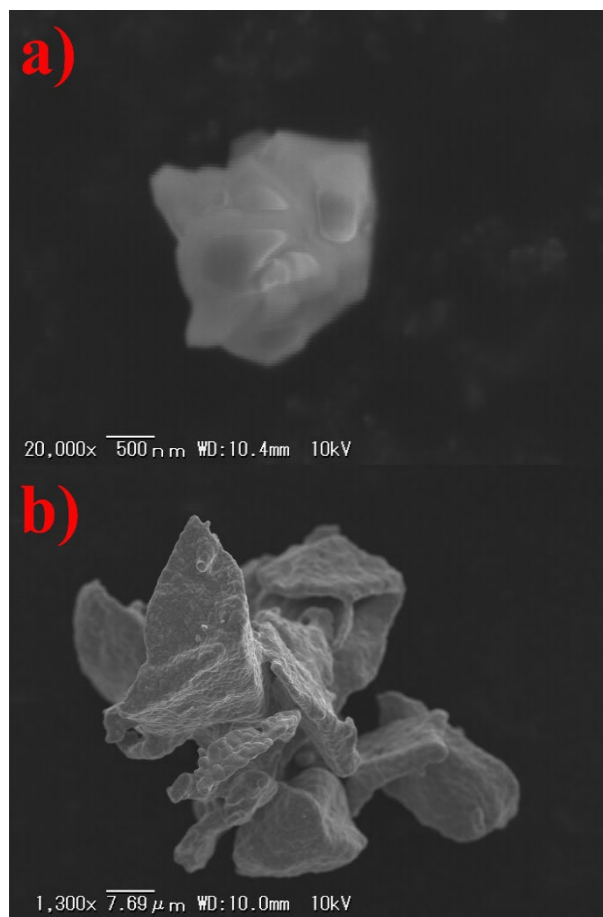

Figure 2. XRD patterns of unused and used catalysts

Figure 3. SEM images of a) before experiemnt b) ratio=1 :4 after experiment catalyst particles

Figure 4. Bio-oil, gas and coke yields from pyrolysis of cellulose for different ratio

3. Results and Discussion

3.1 XRD and SEM analysis

X-ray diffraction patterns of the unused catalysts and used catalyst powder samples are shown in Figure 2 (using 1:1 ratio as an example). Comparing the used catalyst in the experiment and unused catalyst shows the catalyst XRD pattern is unchanged by the pyrolysis experiments, and the catalyst could be recycled. Meanwhile, there are not any spurious diffraction peaks found in the pattern, indicating no other impurity component in catalysts and the sol-gel method is reliable
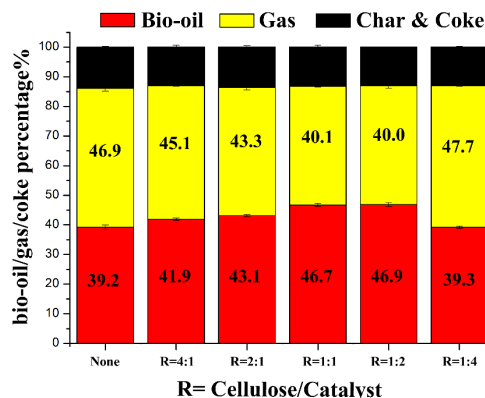
for producing cluster structures. It should be noted that previous literature on the bimetallic catalysts (Ni, Fe) only exhibited a single peak indicating the formation of a Ni– Fe solid solution (Nie *et al*., 2014). The intensity of XRD peaks of the sample in Figure 2 reflects that the formed particles are crystalline and broad diffraction peaks indicate very small size crystallites.

The SEM images are shown in Figure 3 of a typical particle with an uneven surface. From the images a), the particle size is nearly 800 nm, images b) shows the particle is more than 30 μm. It is easy to find that the particle size increases when adding more catalyst. When the catalyst ratio is high, the catalyst has little physical contact with the cellulose, which auto-aggregates at high temperatures.

3.2 Pyrolysis results

3.2.1 Yield results of pyrolysis

The catalysts were mixed with the cellulose directly. The mass of bio-oil and coke were weighed, then the yields were calculated after each pyrolysis experiment. Figure 4 shows the bio-oil mass yields of different ratio. The gas yield is calculated by subtracting the mass of bio-oil and coke from the initial mass of cellulose. Each experiment was conducted more than one time to measure the repeatability.

The bio-oil yield from uncatalyzed cellulose pyrolysis was 39.2% and had a standard deviation of 0.8%. The yield increase as the catalyst is added initially

Table 1. Specific heat capacity (SHC) and heat conductivity coefficient (HCC) for cellulose, Ni metal, Fe metal and cellulose with NiFe catalyst. (SHC , (kJ/kg.K); HCC (W/m. K)) $\bar{X} = \frac{x1fr1+x2fr2}{2}$ $\bar{X}$ used to define the mix HCC of cellulose and

|	SHC (kJ/kg.K)	HCC (200°C) (W/m. K)	HCC (300°C) (W/m. K)	HCC (400°C) (W/m. K)
Cellulose	1.6	0.23		
Ni	0.4	73.3	64.0	59.3
Fe	0.4	61.6	54.7	48.9
Cellulose+Ni$_2$Fe$_3$ (4:1)		13.4		
Cellulose+Ni$_2$Fe$_3$ (2:1)		22.2		
Cellulose+Ni$_2$Fe$_3$ (1:1)		33.3		
Cellulose+Ni$_2$Fe$_3$ (1:2)		44.3		
Cellulose+Ni$_2$Fe$_3$ (1:4)		53.1		

and then decrease: 41.9% for cellulose/catalyst ratio is 4:1; 43.1% for cellulose/catalyst ratio is 2:1; 46.7% for cellulose/catalyst ratio is 1:1; 46.9% for cellulose/catalyst ratio is 1:2; 39.3% for cellulose/catalyst ratio is 1:4. All the ratios used here could improve the yield of bio-oil, which is an important property, because other catalysts have shown to decrease the bio-oil yield, like ZSM-5, ZrO_2 andTiO_2, and silica (Stefanidis *et al*., 2014; Xia *et al*., 2015; Behrens *et al*., 2017).

The reason for bio-oil yield increasing is the difference in specific heat capacity and heat conductivity coefficient. Specific heat capacity is the amount of heat energy required to raise the temperature of a substance per unit and the heat conductivity coefficient is used to measure the property of transferring heat. The specific heat capacity is 1.6 kJ/kg.K for cellulose, 0.44 kJ/kg.K for Ni, 0.45 kJ/kg.K for Fe (The Engineering ToolBox), respectively, which means no matter nickel and iron both can increase its temperature quickly, the heated metal can help transfer heat uniformly for cellulose. Besides, heat conductivity coefficient is different (Madelung and White, 1991) (see Table 1), Ni and Fe is nearly 120 times that of cellulose, which means for cellulose without a catalyst, heat transfer is poor, so some points will increase to high temperature in a short time, which tend to produce gas. However, after adding Ni_2Fe_3 catalyst, the heat conductivity coefficient is enhanced many times, which can help transfer heat well in order to produce more bio-oil (see Table 1). But if add too much catalyst, the HCC is really high, like 53.07 W/m. K, the reaction may more like fast pyrolysis, which means the major product is gas instead of liquid. It is also possible some other reactions took place during the experiment in order to increase the yield, they will be investigated in future work.

From Figure 5, it is shown that the yield of bio-oil changes when the ratio is changing. R=1:2 shows the best bio-oil yield. The reason why the yield reduction is impacted is that when the cellulose ratio is low, the metal catalyst can help transfer heat uniformly and
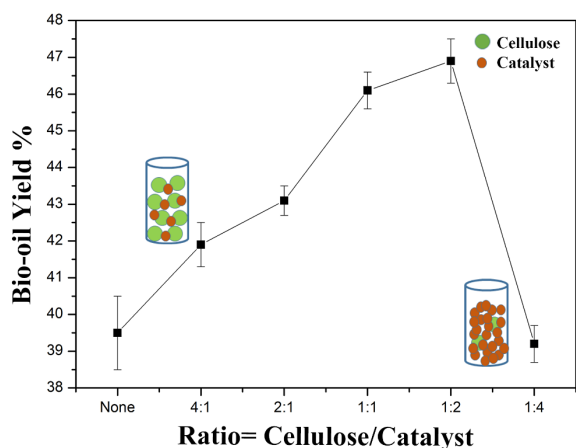
Figure 5. The proposed relationship (inset reactant ratio) between bio-oil yield and the cellulose/catalyst
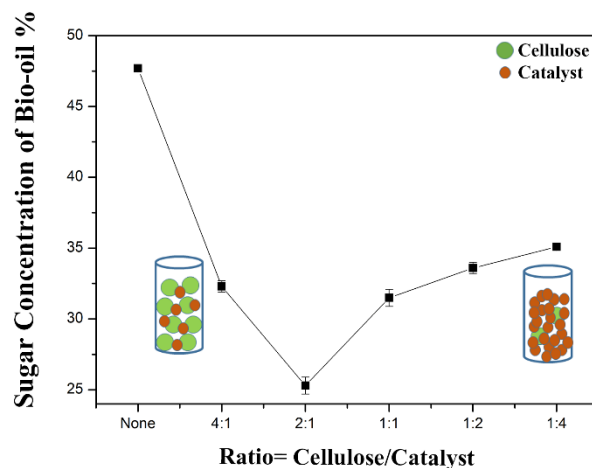
Figure 6. The proposed relationship (inset) between sugar concentration of bio-oil and the

provide sufficient reactive surface (figure inset). However, when the catalyst ratio is high, the catalyst has little physical contact with the cellulose, which auto-aggregates at high temperatures. A high catalyst ratio will decrease the yield of bio-oil.

What conclusion can be drawn? It appears that the R=2:1, 1:1, 1:2 is better when producing bio-oil from cellulose.

3.2.2 GC-MS results of cellulose results

GC-MS was used for analyzing all bio-oil samples produced with the different ratios in order to know the component of the bio-oil. The results of the identified peaks are shown in Table 2. On average, 3% of the peaks were unidentified. All compounds were classified into different groups based on their functional group because of Pyrolysis of cellulose can produce hundreds of compounds. These groups were classified as acids, aldehydes, alcohols, furans, esters, hydrocarbons (HC), ketones, phenols, sugars, and others. Table 2 shows the major products of uncatalyzed cellulose were acids (4.9%), furans (20.7%), ketone (17.5%), and sugars (47.7%). In this study, phenolic compounds were also found in uncatalyzed cellulose pyrolysis, same as other researcher results (Behrens *et al*., 2017); Other main components of the bio-oils derived from noncatalytic and catalytic pyrolysis of cellulose are in good agreement with the literature results (Fabbri *et al*., 2007; Lu et al., 2011; Xia et al., 2015)

In order to examine how the ratio between cellulose and catalyst influence the composition of the bio-oil, each functional group will be discussed herewith. Moreover, the data shows the relationship between the cellulose/catalyst ratio and the bio-oil composition in Figure 6 (Based on averaged data).

First, in Table 2, the data indicate that HC was formed, which is an excellent component to improve the quality of bio-oil, although the percentage is small. No other similar published reports indicate producing HC from cellulose reactants under a nitrogen ambient environment to our knowledge.

Table 2. Composition of cellulose pyrolysis products with different cellulose/catalyst ratio (peak area% of identified peaks, HC is hydrocarbon compounds, unidentifiable compounds were put in others. R=Cellulose/Catalyst)

Sample	Acid%	Alcohol%	Esters%	Furans%	Ketone%	Phenols%	Sugar%	HC%	Others%
None	4.9±0.2	2.3±0.1	2.0±0.1	20.7±0.7	17.5±2.6	1.7±0.4	47.7±0.2	0	2.1±1.2
R=4:1	2.5±0.2	2.9±0.3	2.6±1.0	25.6±0.3	27.4±0.8	1.5±0.1	32.3±0.4	3.6±0.1	1.7±0.4
R=2:1	2.5±0.3	2.8±0.3	1.9±0.3	26.9±0.6	30.7±0.5	1.4±0.5	28.3±0.6	3.3±0.2	2.2±0.5
R=1:1	3.1±0.3	2.3±0.1	2.4±0.2	26.0±.0.7	29.7±0.8	2.2±0.2	31.5±0.6	0.5±0.4	2.4±0.4
R=1:2	3.1±0.2	2.3±0.1	2.6±0.2	23.6±0.5	28.5±1.0	2.7±0.2	33.6±0.4	1.1±0.1	2.4±0.2
R=1:4	3.6±0.1	1.8±0.1	2.3±0.2	19.1±0.6	27.6±0.9	5.2±1.4	35.1±0.2	1.2±0.1	3.7±0.1
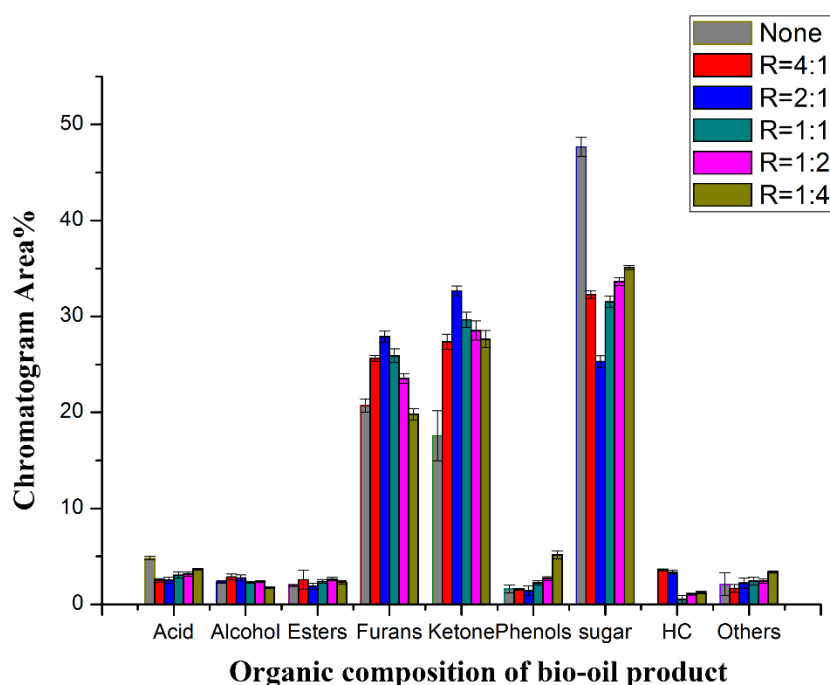
Figure 7. Chemical relative compositions of the bio-oil organic phases with different cellulose/catalyst ratios.

Secondly, all catalysts reduced acid and sugar, which is good for improving the quality of bio-oil. The reason why reducing acid can improve the quality of bio-oil is that the acid can reduce the bio-oil pH value, and make it corrosive to common metals such as aluminum, mild steel, brass and so on. Reducing sugar is important because of its large oxygen content. These results agree well with other literature that the sugar content can be reduced by reactions with catalysts (Wang *et al*., 2016; Behrens *et al*., 2017). Figure 7 shows how the different cellulose/catalyst ratios influence sugar production. The sugar reduction increasing as the catalyst is added initially and then decreases. The reason is that more catalysts can help cellulose decompose well and provide enough surface for reaction, but too much catalyst will auto-aggregate at high temperatures, reducing the reactive surface. So a high catalyst ratio not only decreases the yield of bio-oil but influences the overall catalyst activity based on Figure 7. The ratio = 4:1, 2:1, 1:1 is better for reducing sugar concentration.

Third, when the sugar decreases, the furan, and ketone increase as shown in Figure 7. Cellulose/catalyst ratio of 2:1 shows the best property for increasing ketone and furan compounds because it removes the most mass of sugar. Ketone compounds can change to other hydrocarbon compounds through various methods in order to improve the quality of bio-oil as the chemical reaction advances (King *et al*., 2015; Mehta *et al*., 2015; Ly *et al*., 2017). So it is important to increase the ketone amount for bio-oil.

Finally, all ratios do not affect the alcohol, phenol, and ester amounts. The phenol compounds are usually formed through the secondary reactions from cellulose vapors (Stefanidis *et al*., 2014; Wang *et al*., 2016), that is why it does not change a lot in this study.

4. Conclusion

The Ni_2Fe_3 cluster catalysts were prepared by the sol–gel method successfully and can be recycled. The results show that the cellulose/catalyst ratio will influence the yield and composition of the pyrolyzed bio-oil. The bio-oil yield increases as the catalyst is added initially and then decreases, the R=2:1, 1:1, 1:2 is better for producing bio-oil with high yield. The sugar reduction increases initially and then decreases, in the same manner as the yield. Moreover, R= 4:1, 2:1, 1:1 is better for reducing sugar concentration. Based on the above results, the best cellulose/catalyst ratio is 2:1 or 1:1. This Ni_2Fe_3 cluster catalysts also shows a different reaction pathway when compared to other supported catalysts in the literature, directly catalyze biomass or catalyze the vapors, respectively. In the future, this ratio will be used with other metal cluster catalyst system.

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