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Upgrading Bio-Oil Obtained From Microalgae Over Ni/Biochar Catalyst For Hydrocarbon Synthesis

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ABSTRACT

Upgrading batch process of bio-oil obtained from microalgal biomass was established over Ni/biochar catalyst under hydrogen pressure. Many parameters of the process were investigated including temperature, period of time, content of catalyst based on feedstock weight and agitating condition. The process was gradually improved by changing one parameter while keeping the others constantly. The purpose of the process was to enrich hydrocarbon content in the final liquid product. The Ni/biochar catalyst was synthesized from biochar also obtained from the microalgal biomass, and its characterizations were also provided in this paper or cited in a previous published report. The results revealed that the catalyst had high activity and selectivity in the upgrading process because composition of the liquid product mainly contained hydrocarbons, especially n-heptadecane. This product could be potentially used for blending with commercial diesel fuel. There were also many techniques applied for the characterizations and determination of the catalyst, feedstock and product including XRD, H_2*-TPR, SEM, GC-MS, ASTM methods.*

Keywords: biochar, pyrolysis oil, hydrogenation, biomass, metal supported catalyst.

INTRODUCTION

The bio-oils obtained from pyrolysis process of biomass have been considered as promising sources for biofuel productions in large scale and low cost. However, distribution of oxygen in form of various aliphatic and aromatic oxygenates decreased quality of the bio-oils. Therefore oxygenates had to be reduced as much as possible. Upgrading of the bio-oil through hydrodeoxygenation (HDO), hydrodenitrogenation (HDN), etc., which is similar to hydrodesulphurization (HDS) in oil refining. The HDN, HDO and HDS processes could be assigned as upgrading process of the bio-oil, in which, oxygen, nitrogen and sulfur-containing compounds were converted to hydrocarbons by eliminating corresponding heteroatoms in the form of water, nitrogen and hydrosulfur in the presence of hydrogen and a catalyst. Some of the traditional catalysts were common used in the upgrading process including Co-MoS_2 and Ni-MoS_2. Due to the low sulphur content of bio-oil, a sulphiding agent is typically added to the feed to maintain activity and stability of the catalyst, but this adding could be reduced the activity of the catalysts [1-3].

Recently we have found a new kind of catalyst which could be well effective in the upgrading process for improving characteristics of the bio-oil. The catalyst and the feedstock for the process could be prepared by using biochar and bio-oil both obtained from the pyrolysis of microalgal biomass. Or in other way, we could call this process by close loop process. Therefore, our process consisted of some procedures: pyrolyzing the biomass to obtain bio-oil and biochar; loading suitable metal onto the biochar or modified biochar surface to prepare metal/biochar catalysts and converting the bio-oil to hydrocarbon using this metal/biochar as catalyst. The close loop process could be considerable enhance performance of the upgrading process by reducing the price of the synthesized fuels and avoiding many environment effects.
In a previous published paper [4], we reported the investigation of the catalyst preparation. This paper provided some investigations about the upgrading process over this catalyst.

MATERIALS AND METHODS

Preparation of the Ni/biochar catalyst: The Ni/biochar catalysts were prepared by incipient wetness impregnation method published in a previous paper [4, 5]. The process included some brief steps as followed: pyrolyzing micro-algal biomass for producing biochar and bio-oil 400^oC for 2 hours; impregnating Ni $(NO_3)_2$ at mass percentage of 20% onto refined biochar; calcining the impregnated sample at 400^oC for 4 hours and reducing the calcined product at 400^oC for 3 hours using H_2/N_2 gas mixture. The catalyst was used for upgrading process in purpose of converting the bio-oil to rich hydrocarbon product. The Ni/biochar catalyst was characterized by some techniques such as XRD and H_2-TPR.

Establishing upgrading process on the Ni/biochar catalyst: Bio-oil used in upgrading process was obtained from the pyrolysis of microalgal biomass. The process was performed as following steps:

In the first step, a precise amount of the Ni/biochar catalyst was activated by a reduction process to transfer Ni^{2+} to Ni^0. The reduction process was performed at 300^oC for 3 h in H_2/N_2 flow (10% volume of H_2) of 30 mL min^{-1}.

In the second step, the catalyst was transferred into a stirring supported batch reactor filled with a certain mass of the bio-oil. The H_2/N_2 flow (10% volume of H_2) was maintained during the process. The process was established at certain temperatures for precise times; stirring speed and catalyst dosage were also investigated after obtaining the suitable temperature and time. When the upgrading was finished, the reactor was cooled to room temperature followed by separation of the liquid product from the solid catalyst. The liquid was fractioned for removing water, and then was analyzed by GC-MS for calculating conversion of the bio-oil through the total remained oxygen content in the products in comparison to that of the feedstock.

RESULTS AND DISCUSSION

XRD patterns of the Ni/biochar catalyst in comparison to that of biochar: Figure 1 described the XRD patterns of the biochar and the Ni/biochar catalyst.

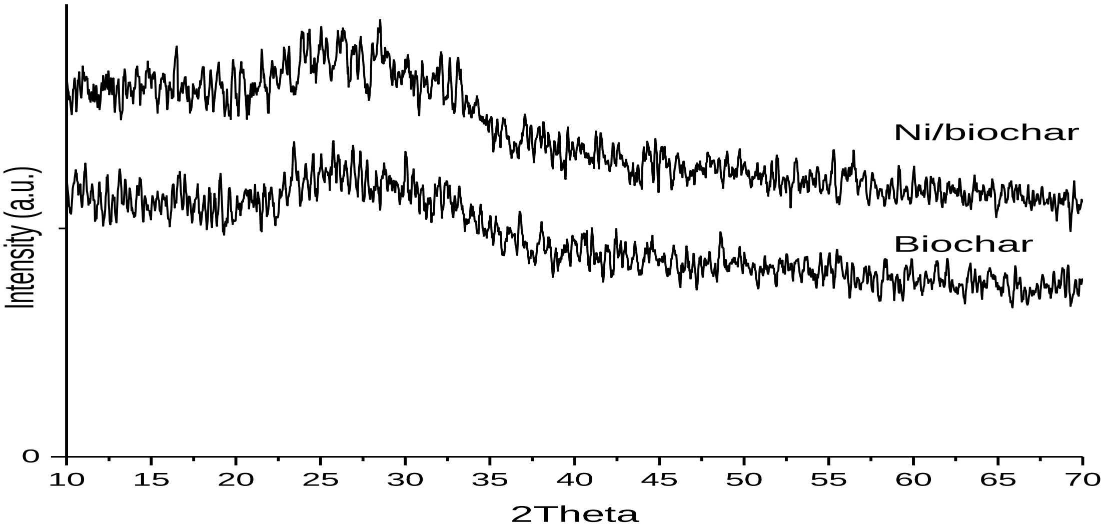

Figure 1. XRD patterns of the Ni/biochar catalysts

The XRD patterns of the biochar and the Ni/biochar catalyst showed similar domination of amorphous structure. There were almost no differences between the two patterns illustrating the incorporation of Ni onto the biochar surface rarely affected the support structure even at a very high content of Ni precursor ($Ni(NO_3)_2$) ~ 20%. There were also no trace of crystalline of NiO, Ni $(OH)_2$ or any kind of Ni based compounds detected in the catalyst demonstrating the very uniform distribution of the Ni particles on the catalyst surface. These phenomena led to an assertion that the Ni portions on the catalyst surface existed in the amorphous phase and well distributed on the surface. The uniform distribution was also an advantage for the activity of the catalyst in the mentioned upgrading process.

H_2-TPR analysis of the Ni/biochar catalyst: Figure 2 described the H_2-TPR result of the Ni/biochar catalyst before reduction, and the peak temperature of reduction and the TCD concentrations were also collected (Table 1).

Generally the peak temperature of reduction of the Ni/biochar catalyst reflected the stability of the Ni^{2+} portions on the catalyst surface as the reduction temperature was lower than 400^{o}C or higher than 500^{o}C corresponding to the reduction of the bulk NiO portions, the Ni-support weak interactions or the Ni-support strong interactions respectively [1-3]. The peak temperature lied between 400^{o}C and 500^{o}C therefore corresponded to the medium interactions of the Ni-support connections.

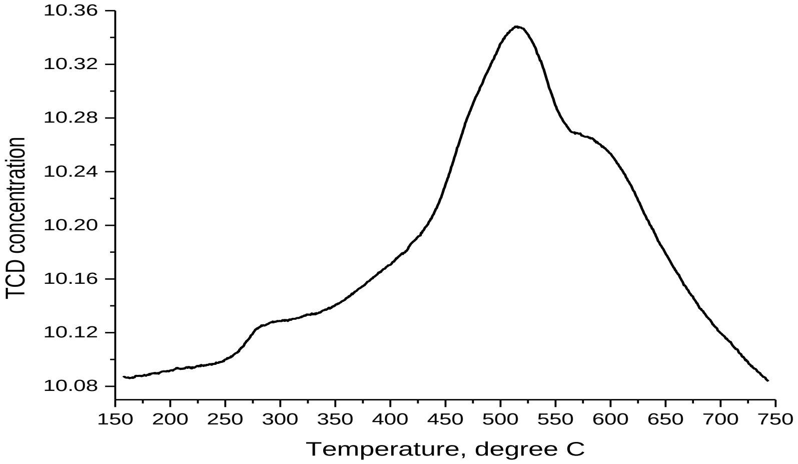

Figure 2. H_2-TPR diagrams of the Ni/biochar catalysts

Table 1. H_2-TPR results of the Ni/biochar catalysts

Type of Ni-support interaction	Reduction peak, °C	H_2 consumption, mmol/g
Weak	288.4	0.06943
Medium	444.2	1.28235
	483.5	0.45003
Strong	522.4	0.68493
	592.5	0.97467
	661.3	0.40975

The results observed from the table1 showed that the existence of the weak Ni-support interactions was minor in comparison to that of the medium and strong Ni-support interactions. The weak Ni-support interaction represented the NiO bulk tending to be agglomerated during the reduction at high temperature, so it was the disadvantage portions for the good distribution of the Ni active sites. On the other hand, the strong Ni-support interactions were poor activity in the reduction process, so the Ni^{2+} content was hardly converted to Ni metal species – the active sites in the upgrading process. Hence, the medium Ni-support interactions were the most adaptive portions for the reduction process. The generated Ni clusters from these interactions could be favorable for the upgrading process because of it good distribution and low level of agglomeration.

On the aspect of H_2 consumption, the total amount of medium and strong interactions were dominant in comparison to that of the weak interactions. The medium Ni-support interactions consumed 1.73238 mmol H_2/g which was approximate to H_2 consumption for the strong interactions of 2.06935 mmol H_2/g. The Ni/biochar catalyst was then applied for the upgrading process using bio-oil as feedstock. This application was described in the next part of the report.

SEM image of the Ni/biochar catalyst: An example of SEM image of the Ni/biochar catalyst was introduced in Figure 3. Observations pointed out that there were some ‘dark regions” on the grey background of the image assigned for the Ni sites diffusing on the biochar surface. The sizes of those sites were unevenly and they varied from 20-50 nm in diameter. These distributions were therefore small enough for nanoscale behavior of the metal sites, and that was good for the catalysts activity.

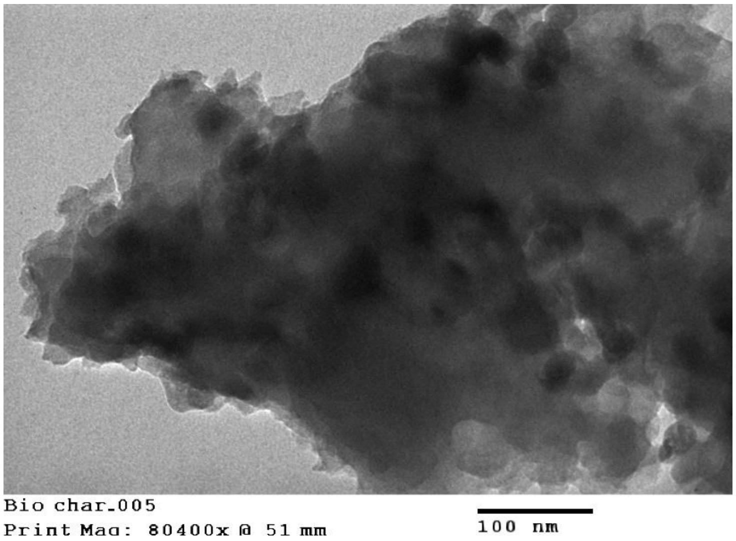

Figure 3. SEM image of the Ni/biochar catalysts

Activity of the Ni/biochar catalyst was also demonstrated in the next part of the report. The upgrading process of the bio-oil obtained from microalgae biomass pyrolysis was established and investigated over the catalyst.

Establishing upgrading process on the Ni/biochar catalyst: Firstly, the specifications of the bio-oil were determined using standard methods, and table 2 described these values.

Table 2. Specifications of the bio-oil

STT	Specifications	Methods	Values
1	Density at 15.5^{o}C	D 1298	0,96
2	Flash point (^{o}C)	D 92	31
3	Viscosity (40^{o}C, mm^{2}/s)	D 445	0,8
4	Pouring point (^{o}C)	D 127	-35,2
5	Distillation	D 86	
	Initial boiling point (^{o}C)		160
	10% (^{o}C)		185
	50% (^{o}C)		265
	90% (^{o}C)		330
	Final boiling point (^{o}C)		335
6	Acid value (mgKOH/g)	D 664	0,53
7	Heating value (MJ/kg)	D 240	29,6
8	Water content (mg/kg)	D 95	18
9	Color	-	Dark, Transparent
10	Odor	-	Special

The specifications of the bio-oil contained many values which was not satisfied for many applications including motor fuels such as low heating value, high water content. The reason could be assigned for its high content of heteroatoms such as oxygen and nitrogen. Secondly, the bio-oil was analyzed to determine its chemical composition before entering the upgrading process. Figure 4 described the GC diagram of the bio-oil.

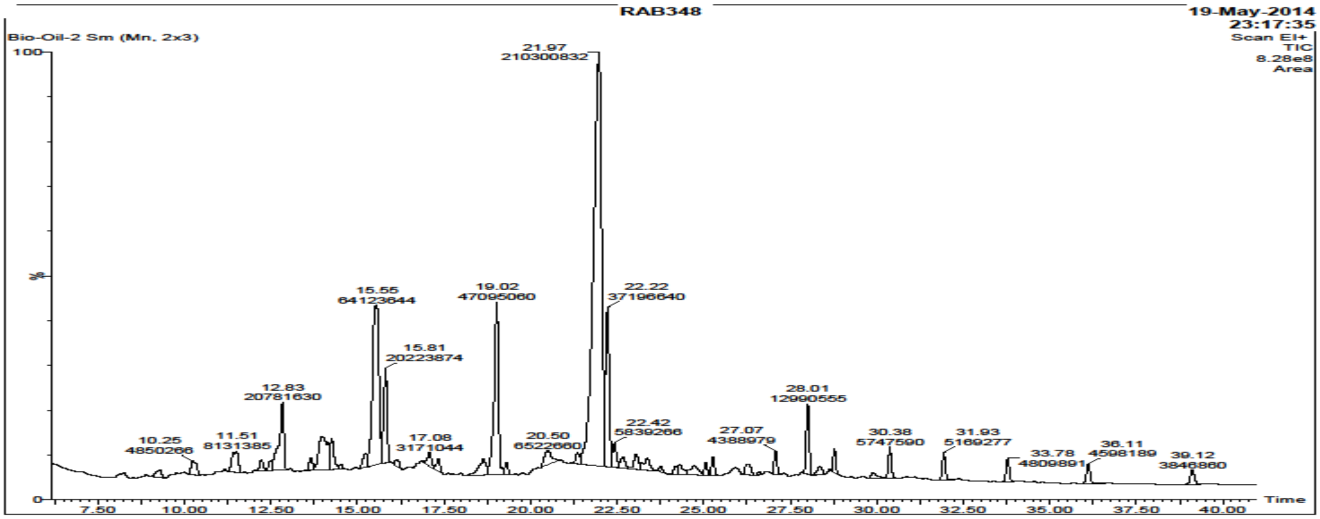

Figure 4. GC diagram of the bio-oil

Table 3. Chemical composition of the bio-oil

No.	*Name*	*Formula*	*Contents, %*
1	Octadecane, 6-methyl-	$C_{19}H_{40}$	0.55
2	4-Trifluoroacetoxytridecane	$C_{15}H_{27}F_3O_2$	1.04
3	Tetradecane, 2,6,10-trimethyl-	$C_{17}H_{36}$	1.75
4	Hexadecane	$C_{16}H_{34}$	4.46
5	9-Hexadecenoic acid	$C_{16}H_{30}O_2$	4.02
6	2-Methyl-E-7-hexadecene	$C_{17}H_{34}$	13.77
7	Heptadecane	$C_{17}H_{36}$	4.34
8	9-Hexadecenoic acid	$C_{16}H_{30}O_2$	0.68
9	Oleic Acid	$C_{18}H_{34}O_2$	2.08
10	Hexadecanenitrile	$C_{16}H_{31}N$	10.11
11	Oleanitrile	$C_{18}H_{33}N$	45.16
12	Octadecanenitrile	$C_{18}H_{35}N$	7.99
13	Oxiraneundecanoic acid, 3-pentyl-, methyl ester, trans-	$C_{19}H_{36}O_3$	1.25
14	1,2-Benzenedicarboxylic acid, diisooctyl ester	$C_{24}H_{38}O_4$	2.79

Table 3 showed the bio-oil chemical composition. The results showed that there were a large amount of oxygenates and nitrogenates which need to be removed through the hydrotreating establishment. There was a distinguishable property of the bio-oil obtained from microalgal biomass than the other biomass: the nitrogen content in the oil was very high in comparison to the oxygen content because the high content of nitrogen element in the original biomass [1, 2].
The investigations of this process were detail described in the table 4.

Table 4. Results obtained from the investigations of the upgrading process

Temperature, ^oC	Value	150	200	250	**300**	350
	Yield, %	20.2	35.2	50.2	**64.2**	64
Time, h	Value	0.5	1	1.5	**2**	2.5
	Yield, %	31.5	49.8	60.1	**68.5**	68.5
Catalyst content, %	Value	2	3	4	**5**	6
	Yield, %	35.9	52.3	61.7	**70.1**	70.1
Stirring speed, rpm	Value	100	200	300	**400**	500
	Yield, %	49.2	54.9	65.3	**71.1**	71.2

The results revealed a collection of optimum parameters such as temperature of 300^{o}C, time of 2 h, catalyst content of 5%wt and stirring speed of 400 rmp. The maximum yield of the process reached 71.1% demonstrating the very high activity and selectivity of the Ni/biochar catalyst. After the upgrading process, the liquid product was also analyzed by GC-MS method to find its chemical composition. These results are presented in figure 5 and table 5.

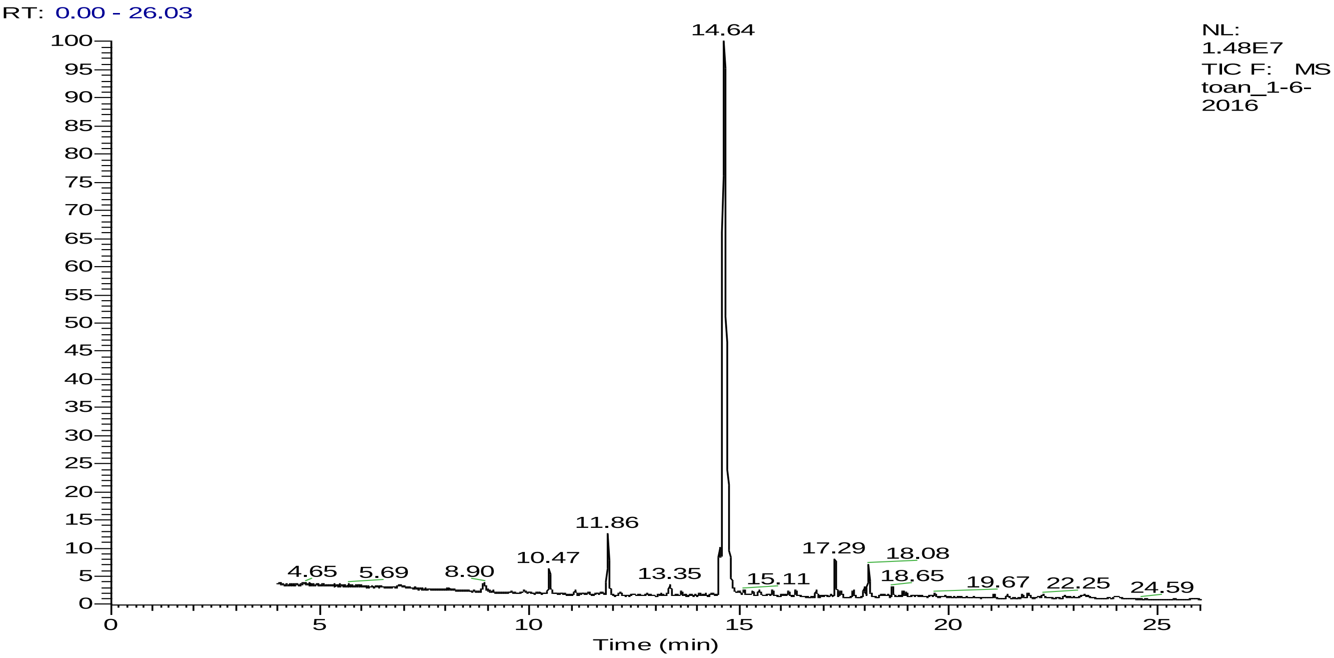

Figure 5. GC diagram of the liquid product obtained from the upgrading process

Table 5. Chemical composition of the liquid product obtained from the upgrading process

No.	*Names*	*Formulas*	*Contents,%*
1	Cyclopentadiene. 5-(1-methylethylidene)-	C_8H_{10}	0.41
2	Decane. 2.6.7-trimethyl-	$C_{13}H_{28}$	0.44
3	Dodecane. 2.6.10-trimethyl-	$C_{15}H_{32}$	1.19
4	Tridecane. 6-propyl-	$C_{16}H_{34}$	1.79
5	Tetradecane. 2.6.10-trimethyl-	$C_{17}H_{36}$	0.39
6	10.13-Octadecadiynoic acid. methyl ester	$C_{19}H_{30}O_2$	0.32
7	cis-(-)-2.4a.5.6.9a-Hexahydro-3.5.5.9-tetramethyl(1H)benzocycloheptene	$C_{15}H_{24}$	0.41
8	Hexadecane	$C_{16}H_{34}$	4.00
9	10-12-Pentacosadiynoic acid	$C_{25}H_{42}O_2$	0.34
10	Octadecadiynoic acid. methyl ester	$C_{19}H_{30}O_2$	0.33
11	Naphthalenone. 7-ethynyl-	$C_{14}H_{18}O$	0.31
12	Tetradecane. 2.6.10-trimethyl-	$C_{17}H_{36}$	1.09
13	Bi-1-cycloocten-1-yl	$C_{16}H_{26}$	0.48
14	**n-heptadecane**	$\mathbf{C_{17}H_{36}}$	**75.68**
15	Naphthalenone. 3.4-dihydro-4.7.8-trimethyl-	$C_{13}H_{16}O$	0.38
16	Naphthalene. 2-butyl-	$C_{14}H_{16}$	0.52
17	Benzocycloheptatriene	$C_{11}H_{10}$	0.66
18	Phenol. 2.4-dimethyl-	$C_8H_{10}O$	0.51
19	Phenol. 2-ethyl-6-methyl-	$C_9H_{12}O$	0.38
20	Cyclonon-4-ynone	$C_9H_{12}O$	2.69

21	Naphthalene. 2.7-dimethyl-	$C_{12}H_{12}$	0.60
22	2.5-Diethylphenol	$C_{10}H_{14}O$	0.61
23	Phenol. 2.4-dimethyl-	$C_8H_{10}O$	3.07
24	6.9.12.15-Docosatetraenoic acid. methyl ester	$C_{23}H_{38}O_2$	0.32
25	Oxiraneoctanoic acid. 3-octyl-. methyl ester	$C_{19}H_{36}O_3$	0.41
26	Bicyclo[4.1.0]heptan-2-one. 3.4.4-trimethyl-3-(3-methyl-1.3-butadienyl)-. [1à.3à(E).6à]-(.+-.)-	$C_{15}H_{22}O$	0.65
27	3-Buten-2-one. 4-(2.6.6-trimethyl-2-cyclohexen-1-yl)-	$C_{13}H_{20}O$	0.6
28	1.8.15.22-Tricosatetrayne	$C_{23}H_{32}$	0.41
29	13-Heptadecyn-1-ol	$C_{17}H_{32}O$	0.52
30	4.5-Dihydroimidazole-4-one. 2-methyl-5-[3-indolylmethyl]-	$C_{13}H_{13}N_3O$	0.49

The hydrocarbon content in the upgraded product reached up to over 80% demonstrating the favorable performance of the reaction. The very high content of n-heptadecane took an advantage of using this kind of product in the diesel fraction. However, there were some tiny amount of many oxygenates and nitrogenates which had to be separated from this product. Therefore it required a purification procedure such as distillation for reduce these heteroatom containing molecules. The Ni/biochar accelerated both HDO and HDN processes, especially reducing the nitrogenates from 63.26% to 0.49%, so this was one of the advanced catalysts for the bio-oil upgrading.

APPLICATIONS

The results show that Ni/biochar accelerates both HDO and HDN processes, especially reducing the nitrogenates from 63.26% to 0.49%. So the method is one of the advanced processes for the bio-oil upgrading catalysts.

CONCLUSIONS

The Ni/biochar catalyst possessed amorphous structure, high content and good diffusion of medium Ni-support connections improving the stability of the Ni species on the catalyst surface. These properties also provide good potential of application in the upgrading process of the bio-oil.

The upgrading process produced liquid product containing a large amount of hydrocarbon, especially n-heptadecane, which was very convenient for blending with diesel fraction. Both oxygenates and nitrogenates were sharply reduced through HDO and HDN processes demonstrating the high activity and selectivity of the Ni/biochar catalyst. However, because of small amount of oxygenates and nitrogenates, the further purification was required for enriching the hydrocarbon content of the product.

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