



Ahmad Nasir Pulungan_2

by Ahmad Nasir Pulungan

THE
Character Building
UNIVERSITY

Submission date: 09-Mar-2023 04:11PM (UTC+0700)

Submission ID: 2032874694

File name: DRAFT_BCAB.docx (1.09M)

Word count: 5986

Character count: 35445

Two Stages Upgrading of Bio-Oil Through Esterification and Hydrodeoxygenation Reactions using Fe₂O₃-CoO Supported Catalyst

Ahmad Nasir Pulungan*

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Jl. Willem Iskandar Pasar V Medan Estate, Medan 20221, Indonesia

Ronn Goei

School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

Agus Kembaren

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Jl. Willem Iskandar Pasar V Medan Estate, Medan 20221, Indonesia

Nurfajriani Nurfajriani

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Jl. Willem Iskandar Pasar V Medan Estate, Medan 20221, Indonesia

Junifa Layla Sihombing

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Jl. Willem Iskandar Pasar V Medan Estate, Medan 20221, Indonesia

Saharman Gea

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Jl. Bioteknologi No. 1, Medan 20155, Indonesia

Hana Ria Wong

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Jl. Willem Iskandar Pasar V Medan Estate, Medan 20221, Indonesia

Muhammad Irvan Hasibuan

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Jl. Willem Iskandar Pasar V Medan Estate, Medan 20221, Indonesia

Rahayu Rahayu

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Jl. Willem Iskandar Pasar V Medan Estate, Medan 20221, Indonesia

Alfred Ting Yoong Tok*

School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

***Corresponding authors:**

Ahmad Nasir Pulungan

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Jl. Willem Iskandar Pasar V Medan Estate, Medan 20221, Indonesia, Fax: (061) 6614002, E-mail: nasirpl@unimed.ac.id

Alfred Ting Yoong Tok

School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore, E-mail: miytok@ntu.edu.sg

Abstract

Bio-oil contains many oxygenated compounds, as well as high acid and water content which can reduce the stability of its components and have poor overall physicochemical properties. In this study, the quality of bio-oil produced from the pyrolysis of oil palm fronds was enhanced through a hydrodeoxygenation (HDO) reaction that was preceded by esterification as a pre-treatment. The catalyst used in the HDO reaction is mixed metal oxide ($\text{Fe}_2\text{O}_3\text{-CoO}$) anchored with zeolite mordenite ($\text{Fe}_2\text{O}_3\text{-CuO/Mor}$). The catalysts were characterized using XRD, SEM-EDX, and BET methods. The presence of metal oxides on the surface of mordenite increases the activity of the catalysts producing liquid products while reducing the formation of coke. Upgrading of bio-oil has improved the physicochemical properties of bio-oil compared to the one-stage upgrading process. The analysis of product showed that the C and H content increased from 11.5 wt% to 23.5 wt%, and from 9.76 wt% to 11.2 wt%, respectively. On the other hand, the O content decreased from 78.7 wt% to 65.2 wt% with a degree of deoxygenation of 59.8%. Moreover, highest heating value (HHV) of the bio-oil increased by 38% from 11.6 MJ/kg to 16.0 MJ/kg.

Keywords: Hydrodeoxygenation, esterification, palm frond bio-oil, Mordenite, metal oxide



1. Introduction

Bio-oil is produced through the pyrolysis process of lignocellulosic biomass. Palm fronds, which contain acidic compounds (acetic acid), phenolic compounds (phenol, 2-methoxy phenol), aldehydes (2-furfural-carboxaldehyde), and ketones (1-hydroxy-2-propanone), are one of the potential biomass resources [1]. However, bio-oil produced from pyrolysis cannot be directly used as fuel because its properties and characteristics have not yet met the required standards [2]. As produced bio-oil is corrosive with high acidity and low heating value due to high water content [3, 4]. Moreover, it is unstable when stored at room temperature due to its high content of oxygenated compounds [5]. Bio-oil is prone to undergo changes as a result of oxidative and thermal degradation during storage [6]. Oxidation causes polymerization and thus increases the viscosity of bio-oil. On the other hand, thermal degradation causes partial decomposition of the components leading to the loss of volatile compounds in bio-oil.

Upgrading the quality bio-oil is important to make bio-oil more compatible for storage and subsequent processing into liquid fuel. Esterification of bio-oils produces bio-oils with greater stability and compatibility during storage, for example, via the formation of compounds like esters, accompanied with further purification processes [4, 7]. Whereas, the conversion of bio-oil to fuel for transportation can be carried out via hydrodeoxygenation (HDO) method. HDO reaction required high operating temperature and pressure. HDO of biomass produces ketones and aldehydes, such as furfural, acetophenone and vanillin, can efficiently enhance the thermodynamic stability of the bio-oil [8]. Two steps upgrading of bio-oil, i.e. esterification and HDO, has currently become a significant research area to develop alternative fuels and high value chemicals [9]. In this case, catalyst is required to make the process faster and effective. So far, HDO process has been developed with numerous strategies, including base catalyzed [10].

Catalysts have played a hugely diverse range of theoretical and practical roles in the development of chemical industries and supporting economic growth since their first introduction to chemical reactions. Heterogeneous catalysts are the most used and developed type of catalysts. Metal-based heterogeneous catalyst, such as Nickel (Ni), Copper (Cu), Rhodium (Rh), Cobalt (Co), and Iron (Fe) and more has been developed for HDO process [11–14]. Cobalt (Co) is a promising catalyst [15], where cobalt oxide catalysts have demonstrated better catalytic performance in a number of reactions among many other transition metal oxides. However, the cobalt oxide catalysts still require modification to improve its catalytic activity, product selectivity, and stability of the catalysts. Iron metal (Fe) is a transition element that has a relatively empty d orbitals, which can increase the total number of active sites of the catalysts [16].

Catalysts can be manufactured by anchoring active metal components on the surface of carriers or support that have large surface areas. Condensation will result in an even distribution of metal across the entire surface of the catalyst and thus improving its overall properties. In comparison to catalysts with no carriers, catalysts with carriers have a better catalytic performance because of the increase in catalysts' surface areas and number of active sites due to the dispersion of active metals onto the catalysts' surface. Materials commonly used as support are silica [17], alumina [18, 19], zeolite [20, 21], and zirconia [22]. Due to its excellent deoxygenation capabilities, zeolite catalyst is the most frequently used catalyst in the biomass conversion process [23]. Mordenite is renowned for its exceptional properties, including high thermal stability because of its ability to keep its structure at 800–900 °C. Mordenite is also ideal as an adsorbent, ion exchange medium, and carrier material because of the presence of voids and channels in its structure [24]. In this work, we aimed to produce heterogeneous catalyst using Co-Fe metal attached to mordenite catalyst by the impregnation method and upgrading bio-oil with two steps esterification and HDO based transition metal oxides and mordenite catalyzed.

2. Experimental

2.1 Materials

The materials used in this study were synthetic mordenite type zeolite (HSZ-640HOA, Tosoh Corporation Japan), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (E. Merck), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (E. Merck), deionized water, ethanol p.a (E. Merck), H_2SO_4 (E. Merck), and KOH (E. Merck). Palm frond waste was obtained from PT. Perkebunan Nusantara II (Percut Sei Tuan district, North Sumatra, Indonesia).

2.2 Preparation of Bio-oil

The conversion of palm frond waste into bio-oil was carried out by semi-fast pyrolysis method. First, the clean palm fronds are mashed into powder, 50 g of powder was put into a reactor. Next, the reactor was set at 500 °C at a heating rate of 1.3 °C/second. Then N₂ gas was flowed at an adjusted flow rate of ±5 mL/sec such that the powder would not be carried away by the gas flow. The pyrolysis process is carried out for 2 h.

2.3 Preparation of Catalyst

Mordenite was thermally activated by calcination at 500 °C under N₂ atmosphere in a fixed-bed reactor. After that, metal impregnation was carried out by the reflux method. Catalyst was prepared by firstly dissolving Co precursor (0.5 g) in 500 mL deionized water in a round bottom flask followed by the addition of 100 g mordenite into the mixture. The mixture was refluxed while constantly stirred at 600 RPM with a magnetic stirrer for 2 h at 80 °C. The condensate was oven-dried at 120 °C to obtain Co/Mor catalyst. Secondly, Mor catalyst was combined into Fe metal precursor solution (1 g/L) and the mixture was refluxed while constantly stirred for 2 h at 80 °C. The condensate was dried in an oven at 120 °C, followed by oxidation process at 500 °C for 2 h with oxygen gas flow (±5 mL/sec) to obtain Fe₂O₃-CoO/Mor catalyst.

2.4 Catalyst Characterization

The crystallography of the catalyst was characterized using X-ray diffraction instrument (XRD Shimadzu 6100). Nitrogen adsorption-desorption test was carried out using gas sorption analyzer. Surface area was calculated using BET method, while pore volume and pore size were analyzed from the desorption band using BJH method. The component mapping of the produced catalyst was analyzed using scanning electron microscope with energy-dispersive X-Ray spectroscopy model series (SEM-EDS Type Zeiss EPOMH 10Zss).

2.5 Upgrading Process

Bio-oil upgrading process is carried out in two stages, starting with esterification followed by the HDO process. Esterification procedure for bio-oil upgrading follows the method reported by Sondakh et al [25], which started by mixing bio-oil and ethanol in a ratio of 1:1 (w/w) into the reactor at 60 °C for 2 h, followed by the HDO reaction with the presence of 1 g of catalyst for 50 g of bio-oils. Both catalyst and bio-oil were put into the fixed bed reactor where N₂ gas was let to flow for 10 minutes to remove the oxygen content in the reactor. Next, the reactor was heated to 450 °C with H₂ gas flowing at 10 mL/min flow rate for 2 h. The product of the reaction was flowed to a cooling hose and weighed. The same procedure is repeated using a Fe₂O₃-CoO/Mor catalyst. The product with the highest yield was analyzed for its components by using GC-MS.

2.6 Bio-oil Characterization

The physicochemical properties of bio-oil before and after the esterification and HDO reactions were compared. The physical and chemical tests carried out were elemental analysis (C,H,N,O) using CHN Analyzer LECO-CHN 628, water content analysis using Metrohm 870 KF Titrano Plus, acid number determination using titration method, higher heating value (HHV) using Sheng and Azvedo formulas, component analysis using gas chromatography-mass spectrometry (GC-MS QP2010 Plus Shimadzu brand), density and viscosity determination using gravimetric method and Ostwald viscometer.

3. Results and Discussions

3.1 Catalyst Crystallinity

The crystallinity of the catalyst samples was examined using the X-ray diffraction. The diffractograms obtained from mordenite and Fe₂O₃-CoO/Mor were compared in Fig. 1. The presence of high-intensity peaks is an indicative of crystalline materials [26]. In this study, synthetic mordenite catalyst used had 100% crystallinity, characterized by high diffraction peaks that were indicated by a narrow, sharp, and intense diffraction peaks located at 6.51; 9.68; 13.52; 19.70; 22.32; 25.69; and 27.62° (JCPDS 06-0239) [27]. Amorphous particles surrounding the crystal can be removed by calcination followed by the introduction of metals into the cavities in mordenite.

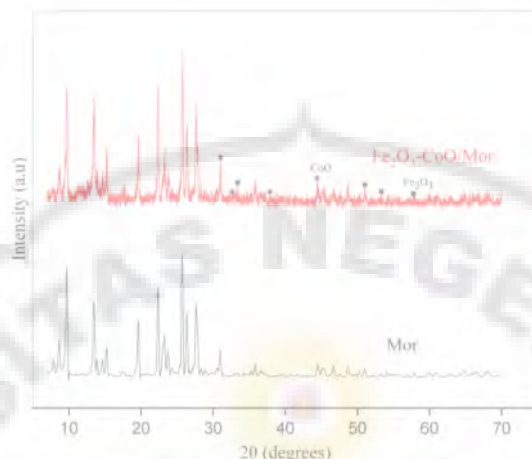


Fig. 1. Diffractogram of mordenite and Fe₂O₃-CoO/Mor catalysts.

The intensity of mordenite is affected by metal loading [28]. The crystallinity of the impregnated metal oxide catalyst is lower than that of pure mordenite. The main peaks of the two catalyst samples formed in the same 2θ (degree) region with varying intensities. The formation of CoO crystal was indicated by the appearance of distinctive peak at 2θ = 30.5; 36.37 and 57.5° which is correlated with the data JCPDS files of 78-431. While the Fe₂O₃ crystal formed were characterized by the appearance of a distinctive peak at 2θ = 31.73; 52.46; and 47.45° in line with the data JCPDS 39-1346. Table 1 shows a comparison of the relative crystallinity of mordenite and Fe₂O₃-CoO/Mor catalysts. The presence of metal oxides into mordenite catalyst did not damage its crystal structure, even though the peak intensity had changed.

Table 1. Comparison of relative crystallinity of Mor and Fe₂O₃-CoO/Mor catalysts

Catalyst	Crystallinity (%)
Mordenite	100
Fe ₂ O ₃ -CoO/Mor	58.07

3.2 Catalyst Morphology and Composition

Surface morphology of the catalysts as observed by SEM analysis is shown in Fig. 2. The SEM micrograph of mordenite showed the presence of different particles which sized varies with the voids between particles. Meanwhile, the surface morphology of Fe₂O₃-CoO/Mor is denser than mordenite. However, there are large lumps due to agglomeration by metal particles.

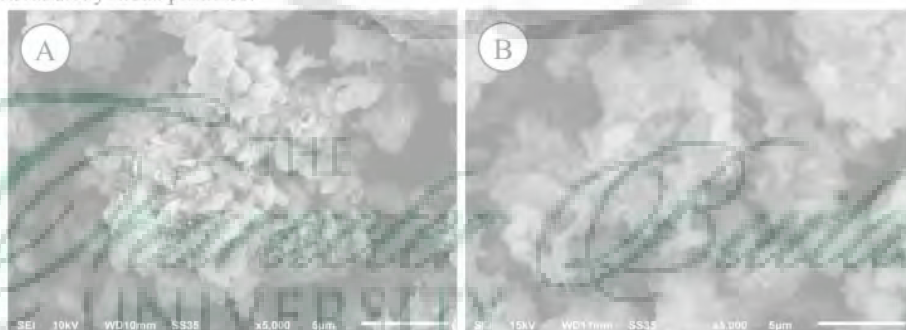


Fig. 2. Surface morphology of (a) Mor and (b) Fe₂O₃-CoO/Mor catalysts.

The results demonstrated that the metals have been evenly distributed throughout the surfaces of mordenite. The average particles diameters of mordenite and Fe₂O₃-CoO/Mor catalysts were 361 nm and 723 nm, respectively. The composition of each catalyst was analyzed using EDX (Table 2). The decrease in Si and Al content of Fe₂O₃-CoO/Mor indicates changes that occur during the metal impregnation, calcination, and oxidation processes. Calcination involved high temperatures process that could cause some of the Si and Al constituents of the skeleton to be separated from the mordenite framework. The increase in the percentage of O due to the oxidation process that forms the transition metal into its oxide form [29].

The Fe and Co metals added to the mordenite to form Fe₂O₃-CoO/Mor catalyst were quantified at 0.38 and 0.2 wt%, respectively. The distribution of Fe and Co metals on the catalyst surface was observed using the SEM-EDX elemental mapping analysis shown in Fig. 3. The two metals are not clearly observed due to its small amount. The elemental distribution shows that the morphology is dominated by Si, Al, and O. The mapping results were in line with EDX data. Impurities in the form of Ni and Cu elements were found in mordenite, but not in Fe₂O₃-CoO/Mor catalyst. Processes, including impregnation, calcination, and oxidation in the preparation of Fe₂O₃-CoO/Mor catalyst have removed the impurities.

Table 2. Mordenite and Fe₂O₃-CoO/Mor catalysts composition

Components	Mordenite (mass%)	Fe ₂ O ₃ -CoO/Mor (mass%)
Si	36.67	30.81
Al	3.15	2.99
O	55.01	57.84
C	4.02	7.78
Fe	-	0.38
Co	-	0.20
Impurities	1.14	-
Si/Al	11.64	10.30

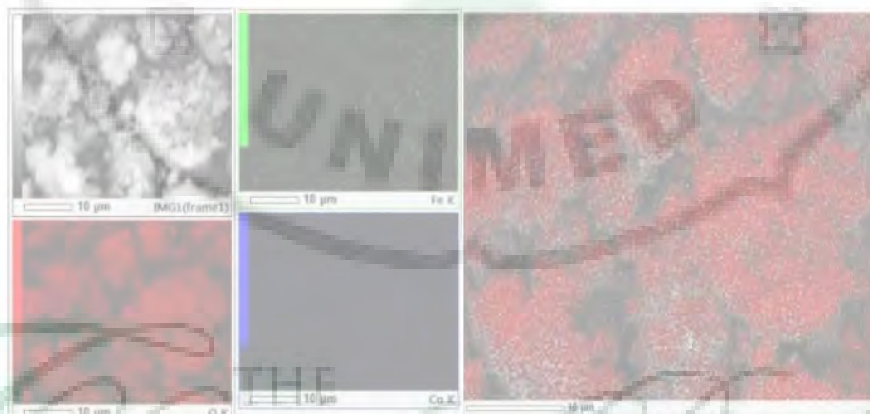


Fig. 3. SEM-EDX elemental mapping of Fe₂O₃-CoO/Mor catalyst. The distribution of elements shows different color for oxygen with red color, iron with green color, and cobalt with blue color.

3.3 Nitrogen Gas Sorption Analysis

The graph of the adsorption-desorption isotherm of each catalyst is shown in Fig. 4. Following the IUPAC classification, the isotherm of Mor and Fe₂O₃-CoO/Mor is classified into type IV with a hysteresis loop at P/P₀ between 0.4-0.9. The presence of a hysteresis loop on the isotherm graph indicates that the material contains mesoporous (2-50 nm) [30].

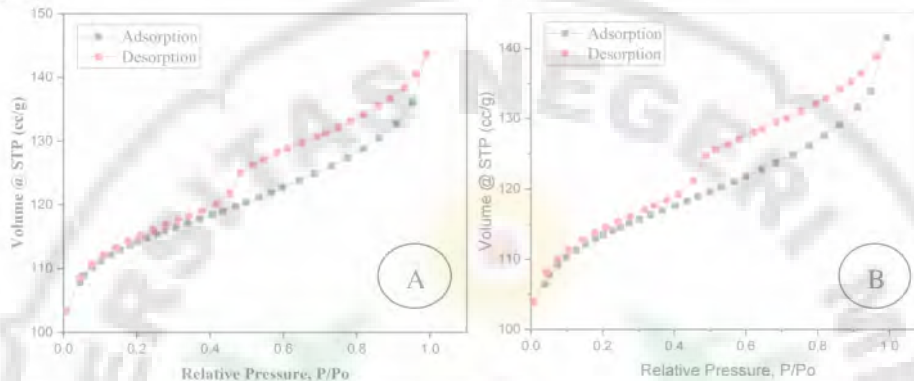


Fig. 4. N₂ adsorption-desorption isotherm graphs of (a) Mor and (b) Fe₂O₃-CoO/Mor catalysts.

The surface area measurement, total volume, and pore diameters of the catalyst samples are summarized in Table 3. The surface area was calculated using BET method, while the total pore volume and pore diameter were analyzed by the desorption band using BJH method.

Table 3. Surface area and pore volume and diameters of mordenite and Fe₂O₃-CoO/Mor catalysts

Catalyst	Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Diameter (nm)
Mor	415.8	0.056	3.755
Fe ₂ O ₃ -CoO/Mor	415.3	0.053	3.782

Fe₂O₃-CoO/Mor catalysts had slightly lower surface area and total pore volume, but slightly larger pore diameter when compared with mordenite. The processing and loading of metal oxides on mordenite has changed the surface and pores of the mordenite catalyst. The calcination process removes inorganic impurities in the pores, hence the improvement in the pore sizes and catalyst characteristic [31]. In addition, the presence of metal oxides on the surface of mordenite which undergoes agglomeration could result in an overall decrease in the surface area of mordenite. The presence of metal oxides can increase the number of active sites of mordenite which can improve the catalytic performance of the catalyst.

3.4 Constituent of the Raw Bio-oil

Pyrolysis at a high temperature causes various compounds to decompose into other compounds. The conversion of biomass in the pyrolysis process goes through various mechanisms, such as char formation, depolymerization, or fragmentation. The formation of char consists of the conversion of biomass in solid residues which present an aromatic polycyclic structure. Depolymerization consists of bond breaking between polymer monomer units. Fragmentation consists of breaking the covalent bonds of the polymer, even within monomer units, and results in the formation of non-condensable gases [32]. Therefore, an analysis was carried out to determine the compounds formed after the pyrolysis process.

The bio-oil obtained from the pyrolysis of palm frond was analyzed for its compound content using GC-MS analysis. The detected compounds were grouped into several groups of compounds such as acids, ketones, furans, alcohols, aldehydes, phenols, and esters which are summarized in Table 4.

Table 4. Composition of bio-oil compounds from palm frond

Group	Compound	Abundance (%)
Furans	2-Furancarboxaldehyde	38.59
	2-Furancarboxaldehyde, 5-methyl-	2.28
		40.87
Phenols	41-nol	4.76
	Phenol, 2-methoxy-	0.39
	Phenol, 2,6-dimethoxy-	1.27
	43	6.42
Ketones	2-Cyclopenten-1-one, 2-hydroxy-3-methyl	0.74
	Cyclopentadecanone, 2-hydroxy-	15.65
		16.39
Acids	Pentadecanoic acid	1.98
	Hexadecanoic acid	12.42
	9-Octadecenoic acid	2.71
		17.11
Aldehydes	Tridecanedial	0.43
	9-Octadecenal	15.88
		16.31

Based on Table 4, the bio-oil content is dominated by furans, ketones, aldehydes, and acids. These compounds are the result of the decomposition of lignocellulose, where cellulose produces furan and ketone groups, hemicelluloses produce many acids and ketones, while lignin produces phenols [33]. These results prove that cellulose and hemicellulose are the most abundant components in palm frond. This is in agreement with previous study which reported that the composition of lignocellulose in biomass generally ranged from 40-50 wt% for cellulose, 20-40 wt% for hemicellulose, and 10-40 wt% for lignin [34].

3.5 Bio-oil Upgrading

The hydroxyoxygenation (HDO) process was carried out on raw bio-oil and esterified bio-oil. Esterification can reduce the acidity of bio-oil by adding polar solvents such as ethanol. It can also reduce density and viscosity and increase the calorific value of bio-oil [35]. The HDO process is carried out to reduce oxygenated compounds in bio-oil to obtain a more stable compounds [36]. In this study, a comparison was made between the direct HDO method and the two-step method that combines the esterification and HDO steps. Upgrading of bio-oil with these two methods was carried out using Mor and Fe₂O₃-CoO/Mor catalysts. The resulting yield distribution is shown in Fig. 5.

THE
Character Building
UNIVERSITY

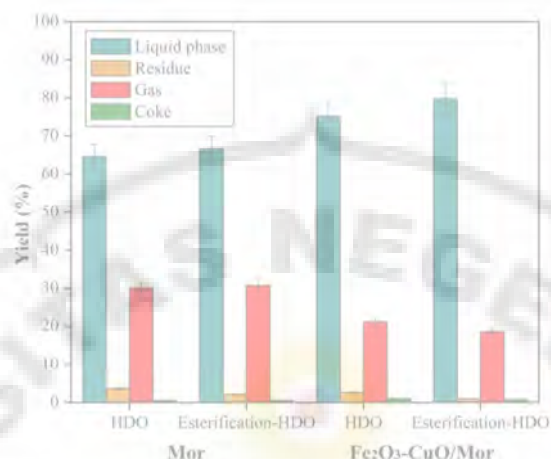


Fig. 5. Product distribution of HDO of bio-oil using Mor and Fe₂O₃-CoO/Mor catalysts.

Based on Fig. 5, in general, more liquid phase is produced from the two-stage esterification-HDO method than using the direct HDO method. Less residue is left when using the two-step method, which indicates a more complete reaction. The esterification step showed a positive impact as a pre-treatment for the bio-oil sample. The conversion was found to be even better when using Fe₂O₃-CoO/Mor as a catalyst. The presence of metal oxide active sites increases the activity of the catalyst to catalyze the bio-oil during the HDO reaction. Grioui et al. [37] explained that the presence of Fe₂O₃ causes the gas produced from the reaction to be inhibited by the condensation reaction and thus moving the gas between the catalyst particles that would result in the increasing residence time for the conversion of the condensed gas and liquid phase products. In addition, there was a decrease in coke formation indicating that the Fe₂O₃-CoO catalyst was effective in inhibiting polymerization and polycondensation reactions [12].

The resulting liquid phase was then analyzed further to determine its physicochemical properties. These properties are compared with the properties of raw bio-oil resulting from pyrolysis and are summarized in Table 5.

Table 5. Physicochemical properties of raw bio-oil, HDO bio-oil, and Esterification-HDO bio-oil

Properties	Raw Bio-oil	HDO	Esterification-HDO
Elemental analysis (wt%)			
C	11.5	17.8	23.5
H	9.76	10.3	11.2
N	0.04	0.03	0.03
O ^a	78.7	71.9	65.2
Water content (%)	75.2	50.1	45.2
Density (g/cm ³)	1.03	1.01	0.93
HHV (MJ/kg) ^b	11.6	13.7	16.0
Viscosity (cP)	1.13	1.10	1.14
Acid number (mg KOH/g oil)	124	112	64
H/C	10.2	6.94	5.69
O/C	5.15	3.04	2.07
DOD (%)		40.9	59.8

^a Calculated by difference in percentage.

^b High heating value was calculated by using the following formula: $HHV (MJ/kg) = -1.3675 + (0.3137 C) + (0.7009 H) + (0.0318 O)$

Based on Table 5, there is a change in the physicochemical properties of bio-oil after undergoing the upgrading process, either through the direct HDO method or the two-stage Esterification-HDO method. Elemental analysis showed that the upgrading process succeeded in increasing the percentages of C and H, as well as reducing O levels. The magnitude of the decrease in O levels can be shown by calculating the degree of deoxygenation (DOD), where the DOD values for the HDO and Esterification-HDO methods are determined to be 40.9% and 59.8%, respectively. In addition, the molar ratio of H/C and O/C can also be determined which could be used to estimate the tendency of the dominant action pathway to be traversed during the upgrading process. In this case, for both methods there was a decrease in the O/C and H/C molar ratios, this indicates the deoxygenation or demethoxylation pathway is preferable over the hydrogenation pathway. Through this reaction pathway, a decrease in O levels can occur due to the release of O as a by-product in the form of H₂O or CO₂. This assumption is supported by GC-MS data which shows the compounds contained in bio-oil. With this analysis elemental data can also be calculated HHV. HHV bio-oil after upgrading process increased from 11.6 MJ/kg to 13.7 MJ/kg (HDO method), and 16.0 MJ/kg (Esterification-HDO method). The 38% increase in HHV value was recorded for the upgraded bio-oils.

Other physicochemical properties that change during the upgrading process are moisture content, density, viscosity, and acid number. The density of bio-oil decreased slightly due to the reduction of large-molecular organic compounds that were converted during the reaction. However, the viscosity of the bio-oil hardly changed. Meanwhile, the water content was reduced by up to a third due to the release of water molecules during the reaction at high temperatures. This also supports the reason for the increase in HHV bio-oil after treatment. Moreover, the acid number is drastically reduced by half, especially in the HDO-Esterification method. This value shows the positive role of the esterification process as the initial stage of the bio-oil upgrading processes. Decreased acid content provides better stability for bio-oil.

3.6 Constituent of Upgraded Bio-oil

The compounds contained in the bio-oil after the upgrading process were analyzed using GC-MS. The compounds contained in bio-oil were categorized into several groups, such as acids, aldehydes, furans, esters, ketones, and phenols as shown in Fig. 6.

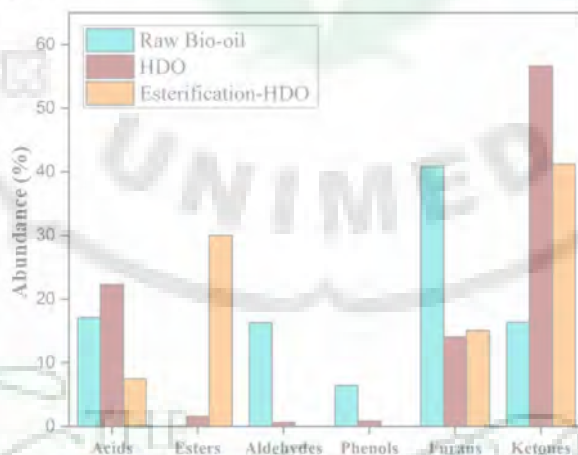


Fig. 6. Bio-oil compound composition after esterification and HDO.

Based on the results from the GC-MS analysis, the compounds in raw bio-oil were dominated by cellulose derivatives including aldehydes, furan, ketones, and lignin derivatives [38]. The upgrading process starting with the esterification stage produces several different components. The esterification step plays an important role in converting acids into esters [39, 40], which is supported by the high percentage of esters up to 30%. By reducing the acids contained in the bio-oil, the stability of the bio-oil improves. This HDO-esterification method also has an impact

on the transformation pathway of furfural compounds (Fig. 7). In this study, furan was one of the dominant compounds found. In the HDO-esterification stage, furfural can go through several reaction pathways as shown in Fig 7. Furfural undergoes cracking causing the furfural bond to break to form acetaldehyde, then in the presence of ethanol, acetaldehyde can undergo aldolization to form ethane,1,1-diethoxy [41]. This compound is an acetal group that can be applied as an organic solvent, starting material for organic synthesis, and fuel additive [42–44]. Furfural can also undergo hydrogenation to produce furfuryl alcohol, then through the hydrogenolysis pathway it produces methylfuran which can then undergo demethylation to release CH₄ to produce furan compounds [45]. Methylfuran is an important chemical compound that has the potential to be used as a fuel component, and as an intermediate in various pharmaceutical and perfume industries [46, 47]. In addition, the ketone group is the most dominant product content. Ketones can be obtained from the rearrangement of furfuryl alcohol in the presence of hydrogen [48] or could also be obtained from ring opening of methylfuran to form open chain ketones [49]. This is supported by the reduced furans content during the upgrading process.

As for the bio-oil which only undergoes one stage of the process through direct HDO, only a very small amount of hydrocarbon compounds are formed in the form of octadecene (0.16%). The presence of octadecene may result from the dehydration of octadecanoic acid contained in the raw bio-oil, through the deoxygenation pathway to produce octadecanal, then through the hydrogenation pathway and undergo hydrogenolysis to produce octadecane [50]. This can not be separated from the role of the catalyst, where the presence of Fe oxide can catalyze the hydrogenation of the C=O bond and inhibit the breaking of the C-C bond during the HDO process. Iron-bearing in the catalyst played important roles by increasing the interaction between Co oxide and mordenite, which stabilized Fe₂O₃-CoO/Mor catalyst during bio-oil HDO reaction. The better the interaction between Co oxide and mordenite, the better the adsorption of oxygenated compounds from raw bio-oil by Fe₂O₃-CoO/Mor catalyst. As a result, there was a not able increase in the conversion reaction rate of the absorbed oxygenated compounds to the desired hydrocarbon compounds [12].

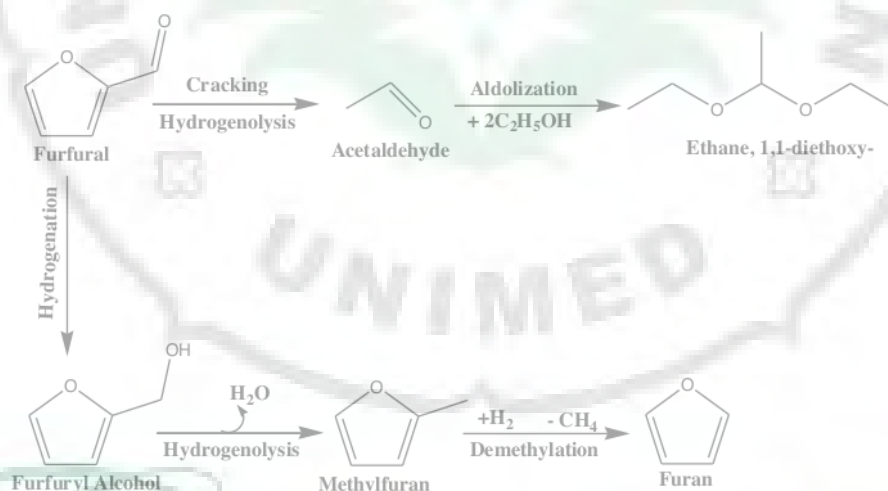


Fig. 7. Possible reactions pathways in Furfural Esterification-HDO process.

4. Conclusions

Upgrading bio-oil using Fe₂O₃-CuO/Mor catalyst with two stages of esterification-HDO has improved the physicochemical properties of bio-oil compared to the one-stage upgrading process. Product analysis showed that the content of C and H increased from 11.5 wt% to 23.5 wt%, and from 9.76 wt% to 11.2 wt%, while O decreased from 78.7 wt% to 65.2 wt% with a degree of deoxygenation of 59.8%. Moreover, HHV increased by 38% from 11.6 MJ/kg to 16.0 MJ/kg. Mixed metal oxide loaded on mordenite increases the number of active sites of the catalyst thereby

increasing the catalytic performance in the HDO process with the catalyst. Meanwhile, esterification provides an active role in reducing acidity by converting carboxylic acids into their ester forms. The upgrading process goes through various reaction pathways, such as hydrogenation, deoxygenation, demethylation, aldolization, and rearrangement. The octadecene hydrocarbon product is produced through the HDO process. In addition, various high value chemicals are obtained during the upgrading process, such as methylfuran and ethane, 1,1-diethoxy.

Statements and Declarations

Ethical Approval Not applicable.

8

Competing Interest The authors declared that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

59

Ahmad Nasir Pulungan: Conceptualization, Methodology, Data curation, Investigation, Writing – original draft. **Ronn Goei:** Conceptualization, Formal analysis, Writing – original draft. **Agus Kembaren:** Formal analysis, Data curation, Writing – review & editing. **Nurfajriani Nurfajriani:** Formal analysis, Writing – review & editing. **Jufia Layla Sihombing:** Formal analysis, Data curation, Writing – original draft. **Saharman Gea:** Supervision, Data curation, Writing – review & editing. **Hana Ria Wong:** Visualization, Investigation, Writing – review & editing. **Muhammad Irvan Hasibuan:** Visualization, Investigation, Writing – review & editing. **Rahayu Rahayu:** Software, Writing – review & editing. **Alfred Iing Yoong Tok:** Supervision, Formal analysis, Data curation, Writing – review & editing.

26

Funding The authors would like to acknowledge the Institute for Research and Community Service (LPPM) Universitas Negeri Medan for the financial support provided through the 2022 Applied Product Research Scheme with grant number No. 104/UN33.8/KEP/PPKM/PT/2022.

2

Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

References

1. Kim SW, Koo BS, Ryu JW, et al (2013) Bio-oil from the pyrolysis of palm and Jatropha wastes in a fluidized bed. *Fuel Process Technol* 108:118–124. <https://doi.org/10.1016/j.fuproc.2012.05.002>
2. Zong R, Li H, Ding WT, Huang H (2021) Highly Dispersed Pd on Zeolite/Carbon Nanocomposites for Selective Hydrodeoxygenation of Biomass-Derived Molecules under Mild Conditions. *ACS Sustain Chem Eng* 9:9891–9902. <https://doi.org/10.1021/acssuschemeng.1c02876>
3. Bridgwater A V. (2012) Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy* 38:68–94. <https://doi.org/10.1016/j.biombioe.2011.01.048>
4. Hu X, Gunawan R, Mourant D, et al (2017) Upgrading of bio-oil via acid-catalyzed reactions in alcohols — A mini review. *Fuel Process Technol* 155:2–19. <https://doi.org/10.1016/j.fuproc.2016.08.020>
5. Wang L, Zhang M, Zhang M, et al (2013) Hydrodeoxygenation of dibenzofuran over mesoporous silica COK-12 supported palladium catalysts. *Energy and Fuels* 27:2209–2217. <https://doi.org/10.1021/ef302166q>
6. Oasmaa A, Kuoppala E (2003) Fast pyrolysis of forestry residue. 3. Storage stability of liquid fuel. *Energy and Fuels* 17:1075–1084. <https://doi.org/10.1021/ef030011o>
7. Ciddor L, Bennett JA, Hunns JA, et al (2015) Catalytic upgrading of bio-oils by esterification. *J Chem Technol Biotechnol* 90:780–795. <https://doi.org/10.1002/jctb.4662>
8. Jiang J, Ding W, Li H (2021) Promotional effect of F for Pd/HZSM-5 catalyst on selective HDO of biobased ketones. *Renew Energy* 179:1262–1270. <https://doi.org/10.1016/j.renene.2021.07.065>
9. Huang H, Zong R, Li H (2020) Synergy effects between oxygen groups and defects in hydrodeoxygenation of biomass over a carbon nanosphere supported Pd catalyst. *ACS Sustain Chem Eng* 8:15998–16009. <https://doi.org/10.1021/acssuschemeng.0c06122>
10. Li L, Dong L, Li D, et al (2020) Hydrogen-free production of 4-alkylphenols from lignin via self-reforming-

- driven depolymerization and hydrogenolysis. *ACS Catal* 10:15197–15206. <https://doi.org/10.1021/acscatal.0c03170>
11. Zhang L, Shang N, Gao S, et al (2020) Atomically Dispersed Co Catalyst for Efficient Hydrodeoxygenation of Lignin-Derived Species and Hydrogenation of Nitroaromatics. *ACS Catal* 10:8672–8682. <https://doi.org/10.1021/acscatal.0c00239>
 12. Cheng S, Wei L, Julson J, Rabnawaz M (2017) Upgrading pyrolysis bio-oil through hydrodeoxygenation (HDO) using non-sulfided Fe-Co/SiO₂ catalyst. *Energy Convers Manag* 150:331–342. <https://doi.org/10.1016/j.enconman.2017.08.024>
 13. Hočevár B, Grilc M, Likozar B (2019) Aqueous dehydration, hydrogenation, and hydrodeoxygenation reactions of bio-based mucic acid over ni, nimo, pt, rh, and ru on neutral or acidic catalyst supports. *Catalysts* 9. <https://doi.org/10.3390/catal9030286>
 14. Bjelić A, Grilc M, Likozar B (2020) Bifunctional metallic-acidic mechanisms of hydrodeoxygenation of eugenol as lignin model compound over supported Cu, Ni, Pd, Pt, Rh and Ru catalyst materials. *Chem Eng J* 394:124914. <https://doi.org/10.1016/j.cej.2020.124914>
 15. Mei J, Zhao S, Xu H, et al (2016) The performance and mechanism for the catalytic oxidation of dibromomethane (CH₂Br₂) over Co₃O₄/TiO₂ catalysts. *RSC Adv* 6:31181–31190. <https://doi.org/10.1039/c6ra00372a>
 16. Satterfield C. (1980) *Heterogenous Catalyst in Practice*. Mc Graw Hill Book, New York
 17. Delucia NA, Jystad A, Laan K Vander, et al (2019) Silica Supported Molecular Palladium Catalyst for Selective Hydrodeoxygenation of Aromatic Compounds under Mild Conditions. *ACS Catal* 9:9060–9071. <https://doi.org/10.1021/acscatal.9b02460>
 18. Vikár A, Solt HE, Novodárszki G, et al (2021) A study of the mechanism of triglyceride hydrodeoxygenation over alumina-supported and phosphatized-alumina-supported Pd catalysts. *J Catal* 404:67–79. <https://doi.org/10.1016/j.jcat.2021.08.052>
 19. Phan DP, Vo TK, Le VN, et al (2020) Spray pyrolysis synthesis of bimetallic NiMo/Al₂O₃-TiO₂ catalyst for hydrodeoxygenation of guaiacol: Effects of bimetallic composition and reduction temperature. *J Ind Eng Chem* 83:351–358. <https://doi.org/10.1016/j.jiec.2019.12.008>
 20. Lee CW, Lin PY, Chen BH, et al (2021) Hydrodeoxygenation of palmitic acid over zeolite-supported nickel catalysts. *Catal Today* 379:124–131. <https://doi.org/10.1016/j.cattod.2020.05.013>
 21. Luo W, Cao W, Bruijninx PCA, et al (2019) Zeolite-supported metal catalysts for selective hydrodeoxygenation of biomass-derived platform molecules. *Green Chem* 21:3744–3768. <https://doi.org/10.1039/c9gc01216h>
 22. He Y, Bie Y, Lehtonen J, et al (2019) Hydrodeoxygenation of guaiacol as a model compound of lignin-derived pyrolysis bio-oil over zirconia-supported Rh catalyst: Process optimization and reaction kinetics. *Fuel* 239:1015–1027. <https://doi.org/10.1016/j.fuel.2018.11.103>
 23. Usui, K., Kidena, K., Murata, S., Nomura, M., & Trisunaryanti W (2004) Catalytic hydrocracking of petroleum-derived asphaltene by transition metal-loaded zeolite catalysts. *J Fuel* 83:1899–1906
 24. Trisunaryanti, W., Triyono, Wijaya, K., Majid, A.B., Priastomo, Y., Febriyanti, E., Syafitri, Hasyiyati & Nugroho A (2012) Characterization and Activity Test of Mordeite and Y-zeolite Catalysts in Hydrocracking of Tire Waste to Fuel Fractions. In: *Prosiding Seminar Nasional Kimia Unesa*
 25. Sondakh RC, Hambali E, Indrasti NS (2019) Improving characteristic of bio-oil by esterification method. *IOP Conf Ser Earth Environ Sci* 230. <https://doi.org/10.1088/1755-1315/230/1/012071>
 26. Pulungan AN, Nurfajriani, Kembaren A, et al (2022) The stabilization of bio-oil as an alternative energy source through hydrodeoxygenation using Co and Co-Mo supported on active natural zeolite. *J Phys Conf Ser* 2193. <https://doi.org/10.1088/1742-6596/2193/1/012084>
 27. Vasconcelos SC, Pinhel LFC, Madriaga VGC, et al (2022) Selective Synthesis of Levulinic Ester from Furfural Catalyzed by Hierarchical Zeolites. *Catalysts* 12:1–18. <https://doi.org/10.3390/catal12070783>
 28. Gea S, Irvan, Wijaya K, et al (2022) Bio-oil hydrodeoxygenation over zeolite-based catalyst: the effect of zeolite activation and nickel loading on product characteristics. *Int J Energy Environ Eng* 13:541–553. <https://doi.org/10.1007/s40095-021-00467-0>
 29. Pulungan AN, Kembaren A, Nurfajriani N, et al (2021) Biodiesel production from rubber seed oil using natural zeolite supported metal oxide catalysts. *Polish J Environ Stud* 30:5681–5689. <https://doi.org/10.15244/pjoes/135615>
 30. Sihombing JL, Gea S, Wirjosenono B, et al (2020) Characteristic and Catalytic Performance of Co and Co-Mo Metal Impregnated in Sarulla Natural Zeolite Catalyst for Hydrocracking of MEFA Rubber Seed Oil into Biotgasoline Fraction. *Catalysts* 10:121

31. Djaeni M, Kurniasari L, Sasongko SB (2015) *International Journal of Science and Engineering (IJSE)* Preparation of Natural Zeolite for Air Dehumidification in Food Drying. 8:80–83
32. Collard FX, Blin J (2014) A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. *Renew Sustain Energy Rev* 38:594–608. <https://doi.org/10.1016/j.rser.2014.06.013>
33. Zhao C, Jiang E, Chen A (2017) Volatile production from pyrolysis of cellulose, hemicellulose and lignin. *J Energy Inst* 90:902–913. <https://doi.org/10.1016/j.joei.2016.08.004>
34. Zadeh ZE, Abdulkhani A, Aboelazayem O, Saha B (2020) Recent Insights into Lignocellulosic Biomass. *Processes* 8:31
35. Xu Y, Zhang L, Lv W, et al (2021) Two-step esterification–hydrogenation of bio-oil to alcohols and esters over raney ni catalysts. *Catalysts* 11:1–10. <https://doi.org/10.3390/catal11070818>
36. Gea S, Hutapea YA, Piliang AFR, et al (2022) A Comprehensive Review of Experimental Parameters in Bio-oil Upgrading from Pyrolysis of Biomass to Biofuel Through Catalytic Hydrodeoxygenation. *Bioenergy Res.* <https://doi.org/10.1007/s12155-022-10438-w>
37. Huang Z, Qin L, Xu Z, et al (2019) The effects of Fe₂O₃ catalyst on the conversion of organic matter and bio-fuel production during pyrolysis of sewage sludge. *J Energy Inst* 92:835–842. <https://doi.org/10.1016/j.joei.2018.06.015>
38. Grioui N, Halouani K, Agblevor FA (2014) Bio-oil from pyrolysis of Tunisian almond shell: Comparative study and investigation of aging effect during long storage. *Energy Sustain Dev* 21:100–112. <https://doi.org/10.1016/j.esd.2014.05.006>
39. Lee HW, Jeong H, Ju YM, Lee SM (2020) Upgrading of bio-oil by ex-situ catalytic pyrolysis and in-line esterification in fluidized bed reactor. *Korean J Chem Eng* 37:1174–1180. <https://doi.org/10.1007/s11814-020-0527-0>
40. Suota MJ, Simionatto EL, Scharf DR, et al (2019) Esterification, Distillation, and Chemical Characterization of Bio-Oil and Its Fractions. *Energy and Fuels* 33:9886–9894. <https://doi.org/10.1021/acs.energyfuels.9b01971>
41. Wang J, Luo Z, Zhang J, et al (2011) Reactions of furfural and acetic acid as model compounds for bio-oil upgrading in supercritical ethanol. 2011 Int Conf Electron Commun Control ICECC 2011 - Proc 2:1587–1592. <https://doi.org/10.1109/ICECC.2011.6067982>
42. Zhang H, Wu Y, Li L, Zhu Z (2015) Photocatalytic Direct Conversion of Ethanol to 1,1-Diethoxyethane over Noble-Metal-Loaded TiO₂ Nanotubes and Nanorods. *ChemSusChem* 8:1226–1231. <https://doi.org/10.1002/cssc.201403305>
43. Kawaguchi D, Ogihara H, Kurokawa H (2021) Upgrading of Ethanol to 1,1-Diethoxyethane by Proton-Exchange Membrane Electrolysis. *ChemSusChem* 14:4431–4438. <https://doi.org/10.1002/cssc.202101188>
44. He X, Liu H (2014) Efficient synthesis of 1,1-diethoxyethane via sequential ethanol reactions on silica-supported copper and H-Y zeolite catalysts. *Catal Today* 233:133–139. <https://doi.org/10.1016/j.cattod.2014.01.023>
45. Gilkey MJ, Panagiotopoulou P, Mironenko A V., et al (2015) Mechanistic Insights into Metal Lewis Acid-Mediated Catalytic Transfer Hydrogenation of Furfural to 2-Methylfuran. *ACS Catal* 5:3988–3994. <https://doi.org/10.1021/acscatal.5b00586>
46. Toledo F, Ghampson IT, Sepúlveda C, et al (2019) Effect of Re content and support in the liquid phase conversion of furfural to furfuryl alcohol and 2-methyl furan over ReOx catalysts. *Fuel* 242:532–544. <https://doi.org/10.1016/j.fuel.2019.01.090>
47. Jaatinen SK, Karinen RS, Lehtonen JS (2017) Liquid Phase Furfural Hydrotreatment to 2-Methylfuran with Carbon Supported Copper, Nickel, and Iron Catalysts. *ChemistrySelect* 2:51–60. <https://doi.org/10.1002/slct.201601947>
48. Moravvej Z, Farshchi Tabrizi F, Rahimpour MR (2021) Vapor Phase Conversion of Furfural to Valuable Biofuel and Chemicals Over Alumina-Supported Catalysts: Screening Catalysts. *Top Catal.* <https://doi.org/10.1007/s11244-021-01470-9>
49. Byun MY, Park DW, Lee MS (2020) Effect of oxide supports on the activity of Pd based catalysts for furfural hydrogenation. *Catalysts* 10:1–10. <https://doi.org/10.3390/catal10080837>
50. Li J, Zhang J, Wang S, et al (2019) Chemoselective Hydrodeoxygenation of Carboxylic Acids to Hydrocarbons over Nitrogen-Doped Carbon-Alumina Hybrid Supported Iron Catalysts. *ACS Catal* 9:1564–1577. <https://doi.org/10.1021/acscatal.8b04967>

Ahmad Nasir Pulungan_2

ORIGINALITY REPORT

29%

SIMILARITY INDEX

22%

INTERNET SOURCES

26%

PUBLICATIONS

7%

STUDENT PAPERS

PRIMARY SOURCES

1	jurnal.ar-raniry.ac.id Internet Source	4%
2	link.springer.com Internet Source	3%
3	www.biofueljournal.com Internet Source	1%
4	ejournal.undip.ac.id Internet Source	1%
5	Saharman Gea, Irvan, Karna Wijaya, Asma Nadia, Ahmad Nasir Pulungan, Junifa Layla Sihombing, Rahayu. "Bio-oil hydrodeoxygenation over zeolite-based catalyst: the effect of zeolite activation and nickel loading on product characteristics", International Journal of Energy and Environmental Engineering, 2022 Publication	1%
6	mafiadoc.com Internet Source	1%

www.mdpi.com

7	Internet Source	1 %
8	research.chalmers.se Internet Source	1 %
9	François-Xavier Collard, Joël Blin. "A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin", Renewable and Sustainable Energy Reviews, 2014 Publication	1 %
10	journal.ugm.ac.id Internet Source	<1 %
11	Jingyun Jiang, Wentao Ding, Hao Li. "Promotional effect of F for Pd/HZSM-5 catalyst on selective HDO of biobased ketones", Renewable Energy, 2021 Publication	<1 %
12	Saharman Gea, Agus Haryono, Andriayani Andriayani, Junifa Layla Sihombing et al. "The Stabilization of Liquid Smoke through Hydrodeoxygenation Over Nickel Catalyst Loaded on Sarulla Natural Zeolite", Applied Sciences, 2020 Publication	<1 %
13	api.intechopen.com Internet Source	<1 %

- 14 www.lookchem.com Internet Source <1 %
-
- 15 pubs.rsc.org Internet Source <1 %
-
- 16 www.researchgate.net Internet Source <1 %
-
- 17 jmrt.com.br Internet Source <1 %
-
- 18 Adistya Husna, Fitria Febrianti, Habibie Syah, Rabiatul Pangaribuan, Tia Surbakti, Junifa Sihombing, Ahmad Pulungan. "Conversion of Cellulose From Palm Oil Middle Waste (*Elaeis Guineensis*) Into Bio-Oil Products As Alternative Fuel", Egyptian Journal of Chemistry, 2022
Publication <1 %
-
- 19 Ali Shemsedin Reshad, Pankaj Tiwari, Vaibhav V. Goud. "Thermo-chemical conversion of waste rubber seed shell to produce fuel and value-added chemicals", Journal of the Energy Institute, 2017
Publication <1 %
-
- 20 Liza Melia Terry, Claudia Li, Jiuan Jing Chew, Aqsha Aqsha et al. "Bio-oil production from pyrolysis of oil palm biomass and the upgrading technologies: A review", Carbon Resources Conversion, 2021 <1 %

21 catalog.lib.kyushu-u.ac.jp <1 %
Internet Source

22 Hao Huang, Rui Zong, Hao Li. "Synergy Effects between Oxygen Groups and Defects in Hydrodeoxygenation of Biomass over a Carbon Nanosphere Supported Pd Catalyst", ACS Sustainable Chemistry & Engineering, 2020 <1 %
Publication

23 Submitted to Indian School of Mines <1 %
Student Paper

24 Saharman Gea, Yasir Arafat Hutapea, Averroes Fazlur Rahman Piliang, Ahmad Nasir Pulungan et al. "A Comprehensive Review of Experimental Parameters in Bio-oil Upgrading from Pyrolysis of Biomass to Biofuel Through Catalytic Hydrodeoxygenation", BioEnergy Research, 2022 <1 %
Publication

25 coek.info <1 %
Internet Source

26 jppipa.unram.ac.id <1 %
Internet Source

27 worldwidescience.org <1 %
Internet Source

- 28 Submitted to University of Hull
Student Paper <1 %
-
- 29 Submitted to KYUNG HEE UNIVERSITY
Student Paper <1 %
-
- 30 getd.libs.uga.edu
Internet Source <1 %
-
- 31 Submitted to International Islamic University
Malaysia
Student Paper <1 %
-
- 32 Meiling Yang, Rongyang Zhao, Jianguang Qin,
Jinyu Zhang, Laishun Yang, Cuiping Wang,
Guangxi Yue. "Co-pyrolysis of heavy bio-oil
and disposable masks pyrolysis with Ce/Fe-
based oxygen carrier catalyst", Fuel, 2023
Publication <1 %
-
- 33 Mingyuan Zhang, Yulin Hu, Haoyu Wang,
Haoyang Li, Xue Han, Yimin Zeng, Chunbao
Charles Xu. "A review of bio-oil upgrading by
catalytic hydrotreatment: Advances,
challenges, and prospects", Molecular
Catalysis, 2021
Publication <1 %
-
- 34 Park, Y.K.. "Effects of operation conditions on
pyrolysis characteristics of agricultural
residues", Renewable Energy, 201206
Publication <1 %
-

35

Yi Wei, Licong Lu, Xudong Zhang, Jianbing Ji. "Hydrogen produced at low temperatures by electrochemically assisted pyrolysis of cellulose in molten carbonate", Energy, 2022

Publication

<1 %

36

Baikai Zhang, Wenzhi Li, Xu Li. "The selectivity depolymerization of corn stover lignin via nickel-doped tin phosphate catalyst in the absence of hydrogen", Industrial Crops and Products, 2021

Publication

<1 %

37

Junifa Layla Sihombing, Saharman Gea, Basuki Wirjosentono, Harry Agusnar et al. "Characteristic and Catalytic Performance of Co and Co-Mo Metal Impregnated in Sarulla Natural Zeolite Catalyst for Hydrocracking of MEFA Rubber Seed Oil into Biogasoline Fraction", Catalysts, 2020

Publication

<1 %

38

Wenchao Ma, Bin Liu, Ruixue Zhang, Tianbao Gu, Xiang Ji, Lei Zhong, Guanyi Chen, Longlong Ma, Zhanjun Cheng, Xiangping Li. "Co-upgrading of raw bio-oil with kitchen waste oil through fluid catalytic cracking (FCC)", Applied Energy, 2018

Publication

<1 %

39

Zhang, Hongxia, Yupeng Wu, Li Li, and Zhenping Zhu. "Photocatalytic Direct

<1 %

Conversion of Ethanol to 1,1- Diethoxyethane over Noble-Metal-Loaded TiO₂ Nanotubes and Nanorods", ChemSusChem, 2015.

Publication

40

F. Toledo, I.T. Ghampson, C. Sepúlveda, R. García, J.L.G. Fierro, A. Videla, R. Serpell, N. Escalona. "Effect of Re content and support in the liquid phase conversion of furfural to furfuryl alcohol and 2-methyl furan over ReOx catalysts", Fuel, 2019

Publication

<1 %

41

Francisco-José Sánchez-Borrego, Noelia García-Criado, Juan F. García-Martín, Paloma Álvarez-Mateos. "Determination of the Composition of Bio-Oils from the Pyrolysis of Orange Waste and Orange Pruning and Use of Biochars for the Removal of Sulphur from Waste Cooking Oils", Agronomy, 2022

Publication

<1 %

42

Lingxiao Li, Lin Dong, Didi Li, Yong Guo, Xiaohui Liu, Yanqin Wang. "Hydrogen-Free Production of 4-Alkylphenols from Lignin via Self-Reforming-Driven Depolymerization and Hydrogenolysis", ACS Catalysis, 2020

Publication

<1 %

43

M D Solikhah, F T Pratiwi, Y Heryana, A R Wimada, F Karuana, AA Raksodewanto, A Kismanto. "Characterization of Bio-Oil from

<1 %

Fast Pyrolysis of Palm Frond and Empty Fruit Bunch", IOP Conference Series: Materials Science and Engineering, 2018

Publication

44

Mario Benés, Rafael Bilbao, Jandyson Machado Santos, Josué Alves Melo, Alberto Wisniewski, Isabel Fonts.

"Hydrodeoxygenation of Lignocellulosic Fast Pyrolysis Bio-Oil: Characterization of the Products and Effect of the Catalyst Loading Ratio", Energy & Fuels, 2019

Publication

<1 %

45

Materials Forming Machining and Tribology, 2016.

Publication

<1 %

46

Wega Trisunaryanti, Karna Wijaya, Triyono Triyono, Anggita Rahma Adriani, Savitri Larasati. "Green synthesis of hierarchical porous carbon prepared from coconut lumber sawdust as Ni-based catalyst support for hydrotreating Callophyllum inophyllum oil", Results in Engineering, 2021

Publication

<1 %

47

Yifeng He, Ronghou Liu, Dominic Yellezuome, Wanxi Peng, Meisam Tabatabaei. "Upgrading of biomass-derived bio-oil via catalytic hydrogenation with Rh and Pd catalysts", Renewable Energy, 2022

Publication

<1 %

48	eprints.nottingham.ac.uk Internet Source	<1 %
49	nbn-resolving.de Internet Source	<1 %
50	tel.archives-ouvertes.fr Internet Source	<1 %
51	uvadoc.uva.es Internet Source	<1 %
52	www.tandfonline.com Internet Source	<1 %
53	"All in One - Complete Issue: ChemInform 32/2014", ChemInform, 2015. Publication	<1 %
54	Advances in Bioprocess Technology, 2015. Publication	<1 %
55	Feng-Li Yu, Yi-Lu Shi, Fang-Zhu Wu, Bing Yuan, Cong-Xia Xie, Shi-Tao Yu. "Aqueous-phase hydrogenation of α -pinene catalyzed by Ni-B alloys loaded on a Janus amphiphilic carbon@silica nanomaterial", Industrial Crops and Products, 2022 Publication	<1 %
56	Junifa Layla Sihombing, Saharman Gea, Ahmad Nasir Pulungan, Harry Agusnar, Basuki Wirjosentono, Yasir Arafat Hutapea. "The	<1 %

characterization of Sarulla natural zeolite crystal and its morphological structure", AIP Publishing, 2018

Publication

57

Junmeng Cai, Md. Maksudur Rahman, Shukai Zhang, Manobendro Sarker, Xingguang Zhang, Yuqing Zhang, Xi Yu, Elham H. Fini. "Review on Aging of Bio-Oil from Biomass Pyrolysis and Strategy to Slowing Aging", Energy & Fuels, 2021

Publication

<1 %

58

Lijun Zhang, Xun Hu, Chao Li, Shu Zhang, Yi Wang, Vahideh Esmaeili, Mortaza Gholizadeh. "Fates of heavy organics of bio-oil in hydrotreatment: The key challenge in the way from biomass to biofuel", Science of The Total Environment, 2021

Publication

<1 %

59

Qinghong Wang, Yi Li, Chelsea Benally, Yiming Li, Chunmao Chen, Zhexuan An, Mohamed Gamal El-Din. "Spent fluid catalytic cracking (FCC) catalyst enhances pyrolysis of refinery waste activated sludge", Journal of Cleaner Production, 2021

Publication

<1 %

60

Yi Wang, Xiang Li, Daniel Mourant, Richard Gunawan, Shu Zhang, Chun-Zhu Li.

<1 %

"Formation of Aromatic Structures during the Pyrolysis of Bio-oil", Energy & Fuels, 2011

Publication

61	article.sciencepublishinggroup.com Internet Source	<1 %
62	biblio.ugent.be Internet Source	<1 %
63	ebin.pub Internet Source	<1 %
64	eprints.utm.my Internet Source	<1 %
65	iopscience.iop.org Internet Source	<1 %
66	neuroquantology.com Internet Source	<1 %
67	scholarworks.montana.edu Internet Source	<1 %
68	spiral.imperial.ac.uk Internet Source	<1 %
69	"Chemical Catalysts for Biomass Upgrading", Wiley, 2020 Publication	<1 %
70	Ali Khosravanipour Mostafazadeh, Olga Solomatnikova, Patrick Drogui, Rajeshwar Dayal Tyagi. "A review of recent research and	<1 %

developments in fast pyrolysis and bio-oil upgrading", Biomass Conversion and Biorefinery, 2018

Publication

71

Lin Hu, Xian-Yong Wei, Zhi-Ming Zong. "Ru/H β catalyst prepared by the deposition-precipitation method for enhancing hydrodeoxygenation ability of guaiacol and lignin-derived bio-oil to produce hydrocarbons", Journal of the Energy Institute, 2021

Publication

<1 %

72

Bingbing Qiu, Xuedong Tao, Jiahao Wang, Ya Liu, Sitong Li, Huaqiang Chu. "Research progress in the preparation of high-quality liquid fuels and chemicals by catalytic pyrolysis of biomass: A review", Energy Conversion and Management, 2022

Publication

<1 %

73

Dinesh Mohan, Charles U. Pittman, Philip H. Steele. "Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review", Energy & Fuels, 2006

Publication

<1 %

74

Jian Mei, Yu Ke, Zhongjue Yu, Xiaofang Hu, Zan Qu, Naiqiang Yan. "Morphology-dependent properties of Co₃O₄/CeO₂ catalysts for low temperature dibromomethane (CH₂Br₂)

<1 %

oxidation", Chemical Engineering Journal, 2017

Publication

75

Jixiang Zhang, Zhongyang Luo, Qi Dang, Jun Wang, Wen Chen. "Upgrading of Bio-oil over Bifunctional Catalysts in Supercritical Monoalcohols", Energy & Fuels, 2012

Publication

<1 %

76

Narayan Lal Panwar, Arjun Sanjay Paul. "An overview of recent development in bio-oil upgrading and separation techniques", Environmental Engineering Research, 2020

Publication

<1 %

77

R. Kumar, V. Strezov, H. Weldekidan, J. He, S. Singh, T. Kan, B. Dastjerdi. "Lignocellulose biomass pyrolysis for bio-oil production: A review of biomass pre-treatment methods for production of drop-in fuels", Renewable and Sustainable Energy Reviews, 2020

Publication

<1 %

78

Shady Abdelnasser, Takumi Hakamata, Hitoshi Ogiwara, Hideki Kurokawa. "Electrochemical Oxidation of 1-Propanol through Proton Exchange Membrane Electrolysis", Journal of Electroanalytical Chemistry, 2022

Publication

<1 %

79

Tomás Cordero-Lanzac, José Rodríguez-Mirasol, Tomás Cordero, Javier Bilbao. "Advances and Challenges in the Valorization of Bio-Oil: Hydrodeoxygenation Using Carbon-Supported Catalysts", Energy & Fuels, 2021

Publication

<1 %

80

Xun Hu, Zhanming Zhang, Mortaza Gholizadeh, Shu Zhang, Chun Ho Lam, Zhe Xiong, Yi Wang. "Coke Formation during Thermal Treatment of Bio-oil", Energy & Fuels, 2020

Publication

<1 %

Exclude quotes

On

Exclude matches

Off

Exclude bibliography

On

UNIVERSITAS NEGERI PADJARAN
UNIMED
THE
Character Building
UNIVERSITY