Research Article

Upgrading Bio-Oil Produced from Corn Cobs and *Cedrela odorata* via Catalytic Olefination and Esterification with 3,7-Dimethyloct-1-ene and Butanol

Folasegun A. Dawodu,[1] **Olubunmi O. Ayodele** ![ORCID],[2] **John O. Akintola,**[1]
Oluwamayokun A. Obembe,[1] **Ameerah O. Sanni,**[1] **and Bosede D. Agbejinmi**[3]

[1]*Department of Chemistry (Industrial), University of Ibadan, Ibadan, Oyo State, Nigeria*
[2]*Department of Forest Products Development and Utilization, Forestry Research Institute of Nigeria, Ibadan, Oyo State, Nigeria*
[3]*Biotechnology Section, Bioscience, Department, Forestry Research Institute of Nigeria, Ibadan, Oyo State, Nigeria*

Correspondence should be addressed to Olubunmi O. Ayodele; bayodele2002@gmail.com

In this study, corn cobs (CC) and *Cedrela odorata* (CO) sawdust which are common waste materials in Nigeria were used as raw materials in the production of bio-oil through pyrolysis at 500°C, for 2 h. The biochar produced in the process was sulfonated with concentrated sulfuric acid under reflux at 150°C for 6 h and used as a solid acid catalyst for bio-oil upgrading. The bio-oil was upgraded by simultaneous olefination and esterification using 3,7-dimethyloct-1-ene and butanol which served as a reagent and cosolvent. FT-IR spectra of the activated biochar from CC and CO raw materials showed an absorbance in the range of $1032–1180 \, \text{cm}^{-1}$, which is indicative of asymmetric S=O bonds, and the spectra also revealed a band between 3400 and $3700 \, \text{cm}^{-1}$, which indicated presence of hydrogen-bonded hydroxyl groups and thus successful activation of the biochar. This observed IR absorbance was absent in the nonactivated biochar. Proximate analysis of upgraded bio-oils revealed a significant reduction in percentage water and oxygen contents, an increase in the high heating value (HHV) and flammability. The chemical composition of the bio-oils was determined using GC-MS, and it showed significant reduction in oxygenated compounds in the upgraded bio-oil as against their high composition in raw bio-oils.

1. Introduction

The world energy demand has increased rapidly in recent years as a result of the steady increase in global population and civilization. We consume vast amount of energy in our industries, high-rise buildings (offices and hotels), and even in our homes just to mention a few. In our everyday lifestyle, we require, consume, and even waste energy. The International Energy Outlook (IEO) backed this up with statistics showing an all-time rise in values of global energy consumption since 2010, despite an increase in global energy production over the years under review [1]. Using computational modeling and analysis, a projected increase in global energy consumption was predicted and alarming values were seen [1]. This requires further exploration into other sources of energy in order to tackle the current high energy demands required for human existence. Energy from renewable resources such as solar, biomass, geothermal, tidal wave, and wind is currently experiencing an increase in growth rate (about 2.6%/year), as reported by International Energy Outlook [1].

Searching for alternative source of energy to fossil fuel at this crucial time is imperative as it provides an escape route from the numerous problems such as global warming, geopolitical friction, and environmental pollution that have originated from the burning of fossil fuels. Wilk et al. [2] highlighted the importance of renewable energy as a means to attain long-term economic sustainability, environmental benefits, and a transformation of the manufacturing and transportation sectors. Subsequently, biomass has been

recognized to possess a promising impact for a projected renewable and sustainable energy future although it is still important to develop technologies which enable the conversion of lignocellulosic and municipal solid waste (MSW) biomass resources into environmentally friendly energy, from a thermodynamic efficiency and system technology standpoints [3]. To achieve a complete transformation of global energy consumption from fossil fuel dependency to renewable energy, a complete paradigm shift to a sustainable development is necessary. Due to the perceived competition of some biomass use with food, the "waste-to-energy" idea was born and energy was generated from waste; technologies have also allowed energy to be obtained from some waste of biomass [4].

Pyrolysis is one of the most frequently used method of bio-oil production from biomass because of its cheap machinery, high yield of product, short time involved in production, ease of machine operation, and flexible production procedure [5]. Three major products are obtained from biomass pyrolysis: liquids (bio-oil or tars), solid (biochar), and low-molecular weight gases (volatiles). The bio-oil produced from pyrolysis contains high water content, high acid value, and low energy density, are unstable overtime, has a foul smell, and are immiscible with conventional hydrocarbon fuel due to high polarity [6]. Mullen and coworkers produced bio-oil and biochar from corn cobs and stover using a pilot-scale fluidized bed reactor. Yields of 60% bio-oil (HHV~20 MJ/kg) and ~18.0% biochar were obtained from the feedstock at an operating temperature of 500°C [7]. Microwave-assisted fast pyrolysis of corn cobs and other agricultural residues were performed, and corn cobs produced the highest yield of bio-oil (42.1 wt.%) with HHV of 22.38 MJ/kg when compared to corn stover, sawdust, and rice straw [8]. A similar study by Biswas et al. [9] also revealed a similar trend when corn cob, wheat straw, rice straw, and rice husk were used under a slow pyrolysis setup. Surprisingly, no report of bio-oil derived from *Cedrela odorata* has been reported in literature. However, bio-oils produced from corn cob and other feedstock contains high moisture content, acid values, and oxygenated compounds, thus limiting their utilization as fuels.

Bio-oil can be subjected to further processes called "upgrading," leading to formation of hydrocarbon fuels having similar physical and chemical properties with conventional fuels [10, 11]. Some methods of upgrading bio-oil include catalytic cracking, high-pressure thermal treatment, catalytic esterification, hydrodeoxygenation, carboxylation, and oxygenation [12], but the esterification reaction represents the cheapest option of bio-oil upgrading.

Esterification is a chemical process to convert the carboxylic acids present in bio-oils to esters, acetals, and ethers by reacting them with alcohols in the presence of an acid or base catalyst [13]. Research has proven that esterification via alcohol addition will reduce the acidity of the bio-oil, thereby improving the quality and stability of bio-oil [14]. More quality fuels can be produced from bio-oil upgrading via simultaneous olefination and esterification reactions. Addition of olefins to the reaction system produces mainly esters and ethers through the reaction of olefin with

carboxylic acids and aldehydes [15, 16]. In this approach, acid-catalyzed addition reactions of carboxylic acids, phenolic compounds, alcohols, and water across olefins all occur simultaneously with esterification producing a bio-oil with enhanced fuel properties [17]. The alcohol added in this reaction functions as a coreagent, reduces phase separation, and increases esterification and acetal formation [18]. Chatterjee and coworkers (2013) employed ethanol and 1-octene as solvents in bio-oil upgrading in the presence of a solid acid catalyst, resulting in a product with low water content and acid value and increased heating value. This is advantageous because hydroxyl group addition across the olefin requires a temperature between 50°C and 130°C [19, 20], which is usually below the temperature required in hydrodeoxygenation or catalytic cracking processes. Thus, catalyst coking and bio-oil polymerization can be avoided [12]. However, the use of the low-cost commodity reagent and solvent ethanol was not as effective as less polar alcohol, 1-butanol, at promoting olefin/bio-oil-phase compatibility [18].

We report a new approach for bio-oil upgrading using simultaneous olefination and esterification reactions, and the catalysts employed were derived from biochar produced after pyrolysis of corn cobs and *Cedrela odorata* sawdust. The biochar was subjected to sulfonation in the presence of concentrated sulfuric acid to produce a solid acid catalyst capable of the one-step upgrading reaction. Bio-oil obtained from corn cobs and *Cedrela odorata* sawdust biomass, having high moisture content and acid value, was subjected to one-pot olefination and esterification reactions using 3,7-dimethyloct-1-ene and 1-butanol as the reactant and cosolvent. The resultant product was characterized using Fourier transform infrared (FT-IR) spectrometer, gas chromatography-mass spectrometer (GC-MS), and proximate analysis to determine bioactive composition and fuel quality.

2. Materials and Methods

2.1. Materials. Sulfuric acid (98.0%), paraffin oil, 1-butanol (99.0%), phenolphthalein, methanol (99.0%), and KOH (90.0%) were obtained from the Department of Chemistry, University of Ibadan. 3,7-Dimethyloct-1-ene (97.0%) was purchased from (J.T. Baker chemicals).

Corn cobs (CO) were obtained from Bodija market, Ibadan, dried at 105°C, and then pulverized using industrial milling machine, while *Cedrela odorata* (CO) sawdust was collected at the sawmill section of Forestry Research Institute of Nigeria (FRIN) Jericho, Ibadan, and then oven-dried at 105°C to constant weight.

2.2. Pyrolysis of Biomass. The experimental setup consists of a double-lagged cylindrical stainless steel reactor equipped with an electrical source and automatic temperature controller. Slow pyrolysis was adopted in the experimental process, and the schematic diagram of the setup is presented in Figure 1. Known grams of CC and CO biomass were weighed and carefully fed into the pyrolysis reactor. The
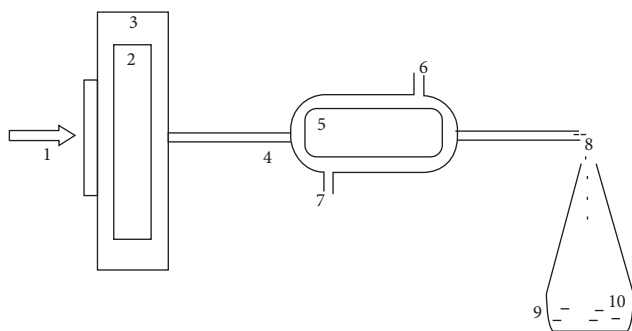
FIGURE 1: Schematic representation of the pyrolysis. 1, feedstock; 2, pyrolytic chamber; 3, furnace; 4, chamber rod; 5, condenser; 6, cold water inlet; 7, cold water outlet; 8, emitted gas; 9, conical flask; 10, pyrolytic oil.

pyrolyzer was operated at a controlled temperature of 500°C for 2 h at 1 atm. The pyrolyzer is equipped with a chamber rod connected to the condenser which cools the vapour, and the product is collected into an air-tight container, while the biochar by-products were collected at the bottom of the reactor.

2.3. Synthesis of Biochar-Based Solid Acid Catalyst.
Biochar produced during pyrolysis of biomass was collected, sieved with a mesh size of 0.5 mm, and further dried at 105°C for 24 h. 20 g of biochar was sulfonated with 200 ml concentrated sulfuric acid in a 1 L round-bottom flask, and the resultant mixture was constantly stirred under reflux at 150°C for 6 h. The product obtained was cooled and then washed with warm distilled water to remove excess sulfuric ions until the pH of the filtrate was neutral (pH 7). Afterwards, the product was dried in the oven at 120°C for 8 h. Incorporation of SO_3H groups on the biochar was confirmed by FT-IR spectroscopy, and the internal structure (amorphous carbon) was determined by the X-ray diffraction technique.

2.4. Solid Acid-Catalyzed Upgrading of Bio-Oil.
Catalytic upgrading of bio-oil was carried out in the presence of solid acid catalysts wherein the catalyst derived from CC biochar was utilized to upgrade bio-oil obtained from CC, while the CO biochar-based catalyst was applied in upgrading of bio-oil obtained from CO sawdust. Simultaneous olefination and esterification reactions were performed in a 250 ml round-bottom flask equipped with the temperature-controlled magnetic stirring system. A known weight of preheated bio-oil (5 g), 23.8 g of 3,7-dimethyloct-1-ene, 1 g of butanol (20 wt.% of bio-oil), and 1 g of sulfonated catalyst was added into the reaction chamber and heated to 140°C under reflux for 6 h. Mass balance calculations were used to estimate the yield of upgraded bio-oil, gaseous products, and char.

2.5. Product Characterization.
The proximate analysis of moisture content, viscosity, density, acid value, pour point, flash point, oxygen content, and flammability was carried out in accordance with the ASTM D3175 standard

procedure. Functional groups were determined with Fourier Transform Infrared Spectrometer (PerkinElmer BX) using KBr pellets.

Chemical composition of bio-oil was determined by GC-MS using Agilent 7890A series with an injector temperature of 270°C and silica capillary column coated with 5% phenyl methylpolysiloxane ($30 m \times 0.32 mm \times 0.25 \mu$). Helium (≥99.9%) was used as the carrier gas. The initial oven temperature of 40°C (hold for 4 min) was used, and the temperature was then ramped at 5°C/min to 250°C and held for 5 min. The dilution solvent used was ethanol with a dilution ratio of 1 : 50.

3. Results and Discussion

3.1. Yield of Bio-Oil.
The percentage yield of bio-oil which represents pyrolysis reaction efficiency is shown in Table 1. The pyrolysis products contain bio-oil, char, and non-condensable gases, and 35.1% bio-oil was obtained from CC while the yield of bio-oil from CO was 34.9%. Since we employed a slow pyrolysis process, the yield of char is usually higher compared to fast pyrolysis. As seen in Table 1, char yields for CC and CO were 34.5% and 34.6%, respectively. However, over 30% of the carbon material was lost as noncondensable gases; thus, the recoverable carbon of over 65% was achieved making the process sustainable, and the gases can be recovered using gas bags, thereby reducing carbon emissions into the environment.

3.2. Characterization of Sulfonated Biochar.
Successful incorporation of SO_3H groups into CC and CO biochar was confirmed using FT-IR (Figures S1–S4), and the IR bands are shown in Tables 2 and 3. Band between 1032 and 1180 cm^{-1} indicates asymmetric S=O stretching, which is observed in the sulfonated biochar that indicates the presence of an acid (H_2SO_4), and also bands between 3400 and 3700 cm^{-1} indicate hydrogen-bonded hydroxyl groups.

The XRD patterns of the raw and acid-modified biochar are presented in Figure 2. The two broad peaks at $2\theta = 10$–32° and $2\theta = 46$–55° were due to the amorphous and graphitic carbon structures, respectively. The structural properties of the biochar did not change upon sulfonation, thus indicating that sulfuric acid did not distort the internal structure of CC and CO. The obtained XRD patterns are in tandem with what have been reported in literatures [21, 22].

3.3. Upgrading Process Using Sulfonated Biochar.
Bio-oil upgrade is exceptionally a complex process because it is composed of a wide variety of oxygenated compounds and in some cases aliphatic or aromatic hydrocarbons and also with substantial amount of water. Sulfonated acid catalyst has been found to exhibit good activity and stability in preliminary catalytic upgrading of bio-oils by simultaneously reacting with alcohols and olefins [16]. The sulfonated catalyst also exhibits a higher water tolerance, thereby allowing complete upgrading as compared to other catalysts form.

Table 1: Products yield of pyrolysis of corn cobs and *Cedrela odorata* biomass.

Sample	Product yield (%)		
	Bio-oil	Char	Gas
Corn cobs	35.1	34.5	30.4
Cedrela odorata	34.9	34.6	30.1

Table 2: Analysis of FT-IR spectra of the raw and activated biochar from corn cob.

S/N	CC biochar	Sulfonated CC	Band assignment
1	461.53		C-H bending
2		606.99	C-O-H bending
3	872.72		C-H out-of-plane bending of benzene derivatives
4		1032.16, 1174.45	S=O symmetrical stretching
5	1437.61	1381.81	In-plane O-H bending and C-O stretch of dimers
6	1602.61	1606.29	C=O stretching vibration for -COOH groups
7	1695.10		C=O stretching
8	2356.22	2352.94	C-H bending
9	2857.14, 2925.16	2857.14, 2929.97	C-H stretching
10	3436.33	3425.73	O-H symmetrical stretching (H-bonded)
11	3770.30		O-H stretching vibration of hydroxyl functional groups

Table 3: Analysis of FT-IR spectra of the raw and activated biochar from *C. odorata*.

S/N	CO biochar	Sulfonated CO	Band assignment
1	458.74		C-H bending
2		617.00	C-O-H bending
3	873.09		C-H out-of-plane bending of benzene derivatives
4		1034.96, 1180.00	S=O symmetrical stretching
5	1441.69	1379.02	In-plane O-H bending and C-O stretch of dimers
6	1596.17	1592.38	C=O stretching vibration for -COOH groups
7	2352.94	2352.94	C-H bending
8	2857.14, 2924.36	2929.97	C-H stretching
9	3440.00	3419.00	O-H stretching vibration of hydroxyl functional groups

The physicochemical properties of bio-oil derived from CC and CO are shown in Table 4. There was no obvious change in appearance of bio-oils before and after upgrading (Figure not shown), but there was a noticeable change from the irritating heavy smoke-like smell of the bio-oil to a sweet-like smell. This is due to the changes from the alkylation of phenolic compounds (phenolic, guiacol, and methyl phenols) and also formation of butyl acetate and esters during upgrading.
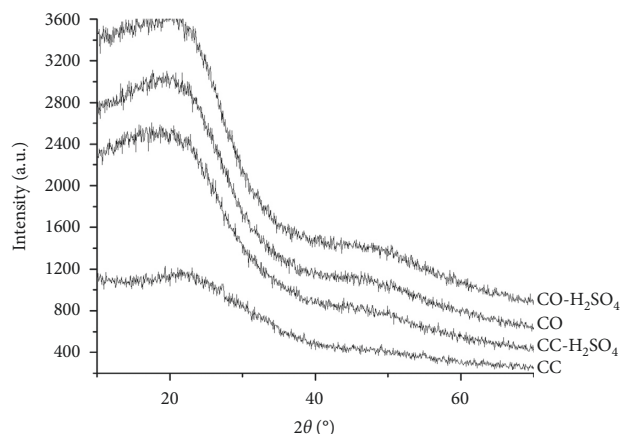

Figure 2: XRD patterns of the raw and acid-modified biochar.

Table 4: Properties of raw and upgraded bio-oil derived from CC and CO.

Parameters	CC bio-oil	CC upgraded bio-oil	CO bio-oil	CO upgraded bio-oil
pH	2.2	3.4	2.4	3.8
Viscosity (kg/m·s) (25°C)	0.1183	0.0586	0.1174	0.0538
Density (kg/m³)	1.30	0.818	1.29	0.806
Acid value (mg KOH/g)	64.52	13.44	60.13	12.24
Flash point (°C)	250	97.5	250	80.5
HHV (MJ/kg)	11.20	32.80	10.10	30.90
Flammability	Low	High	Low	High
Pour point (°C)	−4	−12	−4	−18
Moisture content (%)	30.6	7.4	32.4	8.1
Oxygen content (%)	32.00	21.45	35.40	24.09
Odour	Irritating smell	Sweet smell	Irritating smell	Sweet smell

The water content of the upgraded bio-oil was reduced from 30.6% to 11.4% for CC and from 32.4% to 13.1% for CO. The decrease was due to acid-catalyzed addition of water across the olefin, leading to production of alcohol [16]. This process also removed some portion of water molecules formed during the esterification reaction and ether and acetal formation. This led to the increase in the high heating value of the bio-oil from 11.20 MJ/Kg to 32.80 MJ/Kg for CC and from 10.10 MJ/Kg to 30.90 MJ/Kg for CO. Water removal by acid-catalyzed olefin hydration is the key reason for the successful upgrading process. As water concentration drops, esterification and acetal formation equilibra shift towards ester and acetal products. In turn, the formed ester and acetal and the added alcohol help reduce the phase separation present between the hydrophilic bio-oil and hydrophobic olefin. All of this occurs while maintaining the heating value of raw bio-oil, alcohol, and olefin. Also the presence of residual 1-butanol and 3,7-dimethyloct-1-ene contributes to increase in the heating value of the bio-oil.

The oxygen content was lowered from 32 to 21.45% and from 35.40 to 24.09% for CC and CO, respectively. This reduction helped to increase the heating value and reduce the microphase separation in the bio-oil [23]. The upgraded bio-oil density was lowered from 1.30 to 0.818 kg/m^3 and from 1.29 to 0.806 kg/m^3 for CC and CO, respectively. The pH value of the bio-oil was reduced from 2.2 to 3.4 for CC and from 2.4 to 3.8 for CO. The reduction in the acidity shows that carboxylic acids present in the bio-oil has been converted to esters through the reaction of alcohols and olefin in the presence of the acid catalyst. This improves the quality and stability of the bio-oil [24]. The viscosity of the bio-oil was reduced compared to the upgraded one which shows the influence of the low viscosity of the olefin and the alcohol added. There was an increase in the flammability of the bio-oil which shows the effect of the olefin and alcohol.

3.4. Chemical Composition of Upgraded Bio-Oil. Crude bio-oil has a complex array of highly oxygenated components, which are nearly all oxygenated organic species which includes anhydrous sugars, carboxylic acids, phenols, aldehydes, ketones, mono- and poly-alcohols, ethers, esters, furans, hydroxyl aldehydes, and hydroxyl ketones, which is a major limitation factor [5, 25, 26].

Catalytic olefination and esterification reactions, where olefins and alcohol are added to bio-oil over the solid acid catalyst at low temperature, were employed in this study. The reaction produces mainly esters by the reaction of carboxylic acids, aldehydes, and ketones present in the bio-oil with olefins in the presence of alcohol as a solvent and coreagent. In this process, esterification, olefin hydration, phenol alkylation, etherification, and hydration reactions of olefin occur simultaneously, converting the acid compounds into esters, ethers, and alkylated phenols. The products are less hydrophilic, water is removed instead of being generated, the hydroxyl group was reduced, and oxygen content was reduced, giving a higher fuel value.

Table 5 shows the chemical composition of bio-oil derived from CC and CO biomass as determined by GC-MS analysis. Bio-oil obtained from CC contains mostly oxygenated compounds in form of phenol (37.33%), ester (3.80%), ketones and aldehydes (16.69%), acids (12.57%), alcohols (9.78%), and furans (7.09%), as compared to olefinated CC bio-oil, which contains less phenol (12.82%) and acids (11.03%), but there is an increase in ester formation (46.01%). Likewise, bio-oil obtained from CO also contains more oxygenated compounds: phenol (39.82%) and ketones and aldehydes (21.43%), while ester (2.105%) was considerably low. Upgrading caused an increase in ester (38.12%) and alcohols (11.90), while a decline was noticed in phenol (14.25%), ketones and aldehydes (8.35%), and acids (12.66%). Individual chemical components of the raw and upgraded bio-oils are presented in Tables S1–S4.

Presence of highly oxygenated compounds in the raw bio-oil contributed to its nonsuitability as automobile fuels. Therefore, reduction in the oxygenated compounds, acid content, and increase in esters show a high catalyst activity, leading to lower viscosity and hydrophilicity of the final

TABLE 5: Chemical composition of raw and upgraded bio-oil from biomass.

Components	CC raw bio-oil (%)	CC upgraded bio-oil (%)	CO raw bio-oil (%)	CO upgraded bio-oil (%)
Acids	12.57	11.03	17.05	12.663
Esters	3.80	46.01	2.105	38.12
Phenols	37.33	12.82	39.82	14.253
Ketone and aldehyde	16.69	5.62	21.43	8.35
Alcohol	9.78	11.52	0	11.898
Furan	7.09	0.41	5.99	0
Octene	0.00	12.58	0	14.714
Others	5.76	0.00	4.165	0

product. These changes increase both stability and hydrocarbon blending ability of the upgraded bio-oil. These results showed that 3,7-dimethyloct-1-ene/butanol upgrading is feasible and produces less hydrophilic fuel molecules, which makes the olefinated bio-oil suitable for fossil fuel substitution.

4. Conclusion

Upgrading of pyrolyzed bio-oil obtained from corn cob and *Cedrela odorata* (sawdust) by catalytic olefination and esterification using 3,7-dimethyloct-1-ene in the presence of butanol with the solid sulfonated catalyst prepared from the biochar by-products was investigated to improve the properties of the crude bio-oils obtained and make it a suitable substitute for conventional fossil fuel. The change in the high heating value was moderate, in the presence of excess olefin which reduced the water content significantly. However, butanol helped to decrease acid content of starting raw bio-oil by formation of esters. Therefore, butanol remains a key component in catalytic olefination for bio-oil upgrading. The FT-IR analysis of the crude and catalyzed biochars shows the sulfonation and hydroxyl peak, indicating the suitability of the catalyzed biochars for the catalysis process. The GC-MS analysis results show that the crude bio-oil was dominated by oxygenated compounds, while the catalytic olefination and esterification bio-oil are dominated with desirable compounds such as esters and phenolics, thereby showing a lower percentage of undesirable acidic compounds. The proximate analysis results showed the acid-catalyzed olefination and esterification of the crude bio-oil in the presence of butanol were able to reduce the water content and acid value and thus increased the heating value and calorific value of the bio-oil. This study has further confirmed the assertion that catalytic olefination and esterification can significantly improve the fuel properties of bio-oil in the presence of some requisite such as alcohol and catalyst.

Data Availability

The data used to support the findings of this study are included within the article and also included within the supplementary information file(s). Furthermore, data of this study are available from the corresponding author upon request.

Conflicts of Interest

Acknowledgments

Supplementary Materials

Table S1: selected organic oxygen-containing components of raw bio-oil (corn cobs). Table S2: selected organic oxygen-containing components of upgraded bio-oil (corncobs). Table S3: selected organic oxygen-containing components of raw bio-oil (*Cedrela odorata*). Table S4: selected organic oxygen-containing components of upgraded bio-oil (*Cedrela odorata*). Figure S1: FT-IR spectra of raw corn cobs. Figure S2: FT-IR spectra of the corn cobs catalyst. Figure S3: FT-IR spectra of raw *Cedrela odorata*. Figure S4: FT-IR spectra of the *Cedrela odorata* catalyst. (*Supplementary Materials*)

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