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Microwave-assisted Esterification of Tall Oil Fatty Acids with Methanol Using Lignin-based Solid Catalyst

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Abstract

During alkaline pulping significant amounts of lignin, carbohydrates (mostly hemicelluloses), and extractives (tall oil soap and turpentine) are removed from wood feedstock. In this study, the catalytic esterification of fatty acids in tall oil with methanol to produce fatty acid methyl esters under microwave irradiation was performed at 100 °C for 10-60 min. A novel heterogeneous acid catalyst tested for this purpose was synthesized from the hardwood alkali lignin that was precipitated by acidification from the black liquor from soda-AQ pulping. The comparative reaction data were obtained by using other solid catalysts, Amberlyst 15 and *p*-toluenesulfonic acid. The results showed the highest esterification yields 93, 88, and 80 % with the *p*-toluenesulfonic acid, lignin-based, and Amberlyst 15 catalysts, respectively, at 100 °C with a reaction time of 60 min and the corresponding yield without catalyst was 20 %. It was also observed that the lignin-based catalyst could be easily recovered and reused without any notable deactivation.

1 Introduction

Biofuels have recently gained significant attention because of their environmental benefits and gradually increasing scarcity in fossil fuels.¹⁻³ They are non-toxic, renewable, and biodegradable fuels that traditionally consist of fatty acid (m)ethyl esters (FAMEs or FAEEs).^{4,5} The benefits towards their use also include sustainability, reduction of greenhouse gas emissions,³ and can be directly used in the existing engines without any practical modifications.^{1,6} However, raw material and production costs form the major limitation on the growth of industrial-scale biofuel production.^{7,8} For this reason, clearly more research to exploring novel ways towards the sustainable and economically feasible production methods is still needed. Especially, the further development of stable, heterogeneous, and recyclable catalysts, being based on low-cost and wide-scale available feedstocks and, on the other hand, on their effective production methods with minimal energy consumption would be of benefit.

The extractives such as non-volatile crude tall oil (CTO) soap and volatile crude turpentine, as well as the cooking liquor ("black liquor", BL) that contains mostly lignin and carbohydrate-derived aliphatic carboxylic acids, comprise the by-products obtained from alkaline pulping.⁹ Carboxylic acids (i.e., fatty and resin acids) in the CTO soap are liberated by adding sulfuric acid and the CTO formed is purified and fractionated by vacuum distillation to obtain various commercial products including tall oil fatty acids (TOFAs) and tall oil rosin (TOR) together with light oil, distilled tall oil (DTO), and tall oil pitch.⁹⁻¹² In contrast, BL is evaporated and burned in a recovery furnace to generate energy and recover the inorganic cooking chemicals. In spite of the modern delignification and recovery processes, alkaline pulping is facing major challenges and will need to find new products with a moderate added value in order to remain competitive.

Extensive research has been devoted to produce biodiesel from the CTO-derived fatty acids;^{5,13,14} for example, a wide range of investigations has been conducted on the utilization of homogeneous and heterogeneous acid catalysts for esterifying fatty acids. The major drawback of the use of soluble homogeneous catalysts lies in their reusability and, on the other hand, in the purification of products.^{15,16} Therefore, in recent years, much attention has also been paid to the use of recyclable solid catalysts, although they may be easier to deactivate over time, leading to a loss of both productivity and reaction selectivity compared to the use of homogeneous catalysts. Normally, relatively expensive carbohydrate-based biomass has been used as raw material for producing solid acid catalysts.^{15,17-19} In

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3 contrast, economically a more attractive approach would be to use by-product alkali lignin for
4 this purpose. However, at present only limited literature data are available on the production
5 of lignin-based solid catalysts and their applications.^{20,21}
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8 The main aims of this study (Figure S1) were i) to prepare and characterize a
9 solid acid catalyst from alkaline lignin by the phenol formaldehyde condensation reaction
10 followed by the sulfonation reaction and ii) to produce FAMEs from TOFAs and methanol
11 under microwave irradiation by means of this lignin-based catalyst.
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15 16 **2 Materials and methods**

17 18 19 **2.1.1 Catalyst preparation**

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22 The lignin-based acid catalyst was prepared from the precipitated hardwood
23 (birch, *Betula Pendula*) lignin obtained by acidification (pH to about 2) of hardwood soda-
24 AQ BL.^{22,23} In the preparation of catalyst, the initial washed and dried lignin (3 g) was
25 dissolved in 12 mL of distilled water in a round bottom flask. The solution was then mixed
26 with 2.4 mL of formaldehyde and 5 mL of hydrochloric acid (37 %). The slurry formed was
27 immersed in an oil bath (90 °C) under stirring for 5 h. After the phenol formaldehyde
28 condensation reaction was completed, the solid was separated by filtration and dried at 105
29 °C for 4 h.²⁰ The sulfonation reaction was carried out by adding the sample into 10 mL
30 concentrated sulfuric acid,²³ and the suspension was stirred at 150 °C for 2 h. The black solid
31 material was filtered and thoroughly washed repeatedly with hot and cold water until no
32 sulfur-containing were detected in the wash water. The final product was dried at 105 °C and
33 was evenly crushed with a mortar.
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44 45 **2.1.2 Catalyst characterization**

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47 The molar amount of -SO₃H per gram of lignin catalyst (indicated as M-SO₃H)
48 was determined by acid-base titration that was modified from the literature.²⁰ In this
49 determination, the aqueous 2 mol/L sodium chloride solution (20 mL) and the lignin catalyst
50 (0.1 g) were mixed in an Erlenmeyer flask and the mixture was sonicated for 1 h and filtered.
51 The solution was then titrated with the standardized 0.1 mol/L sodium hydroxide solution
52 using phenolphthalein as an indicator. The total molar amount of acid groups -SO₃H, -CO₂H,
53 and -OH (i.e., the sum of M-SO₃H, M-CO₂H, and M-OH) was determined by acid-base
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3 titration described in the literature.²⁴ In this determination, about 0.1 g of lignin catalyst was
4 added to 40 mL 0.1 mol/L NaOH and the solution was then shaken for 4 h and filtered. The
5 solution was back titrated with the standard 0.1 mol/L HCl solution using a pH meter and
6 thus, the amount of the NaOH consumed corresponded to the total amount of acid groups. In
7 the third determination, about 0.1 g of lignin catalyst was added to 25 mL of 0.08 mol/L
8 NaHCO₃ solution and this solution was sonicated for 2 h and filtered. The solution was then
9 titrated with 0.1 mol/L HCl to pH 3.9 resulting in the total molar amount of acid groups -
10 SO₃H and -CO₂H (i.e., the sum of M-SO₃H and M-CO₂H), which was obtained from the
11 NaHCO₃ consumed. Finally, M-OH was obtained by subtracting Σ M-SO₃H+M-CO₂H from
12 Σ M-SO₃H+M-CO₂H+M-OH.
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20 The elemental composition of lignin catalyst was examined using a scanning
21 electron microscope EVO-50 (Carl Zeiss AG, Oberkochen, Germany) equipped with an
22 energy dispersive X-ray spectrometer (Bruker GmbH, Germany) (SEM-EDX). The results
23 were handled with the Bruker Quantax. For the determination, the samples were dried and
24 impacted on 12 mm carbon tape (Pelco Tabs, Ted Pella, CA, USA) over a sample stub. The
25 samples were analyzed with a magnification of 167 \times and X-ray spectra were acquired for a
26 live time of 90 s over an energy range of 0-10 kV (with a beam current of 30 μ A and an
27 accelerating voltage of 10 kV).
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33 FT-IR spectra of lignin catalyst were recorded with a Tensor27 FT-IR
34 spectrometer (Bruker GmbH, Germany). The spectra were taken as an average of 32 scans
35 with a resolution of 4 cm⁻¹ in the wave number between 400 cm⁻¹ and 4000 cm⁻¹. The results
36 were handled with the Bruker Opus version 6.5 software.
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41 2.1.3 Analysis of fatty and resin acids

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45 For quantitative analysis of compounds in the commercial fraction of TOFAs
46 (Forchem Oy, Finland), the sample was diluted with acetone (0.5 mg/mL) and derivatized at
47 70 °C for 1 h for a gas chromatography system equipped with a flame-ionization detector
48 (GC/FID) with a mixture of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and
49 trimethylchlorosilane (TMCS) (99:1 v/v). An Agilent 6850 Series GC System (Agilent
50 Technologies, Santa Clara, CA, USA) with an Equity-5 (30 m \times 0.32 mm i.d., film thickness
51 0.25 μ m) column was used. The injector temperature was 290 °C and the detector
52 temperature was 300 °C. The GC oven temperature program was 1.5 min at 100 °C, followed
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3 by an increase of 6 °C/min to 180 °C, 10 min at 180 °C, an increase of 4 °C/min to 290 °C,
4 and 20 min at 290 °C. The relative mass-based response factors used between the GC peak
5 areas derived from the internal standard heneicosanoic acid and those of compounds were
6 equal to 1. Qualitative analysis of the individual components was performed with an Agilent
7 6890 Series GC System equipped with a 7683 injector and an Agilent 5973 mass selective
8 detector (GC/MSD). In this case, the capillary column used was an HP-5MS (30 m × 0.32
9 mm i.d., film thickness 0.25 µm) and the GC oven temperature program was the same as that
10 used in the quantitative analyses.
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17 18 **2.2.4 Microwave-assisted esterification** 19

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21 Before esterification the TOFAs were pretreated in an oven at 65 °C for 2 h. In
22 the esterification experiments about a 1.4-g mixture of TOFAs was added to 0.48 g of
23 methanol (molar ratio 1:3) in the presence of 5 wt% a solid lignin catalyst. The reaction was
24 carried out at 100 °C for 10 min to 60 min in a microwave reactor (CEM-Discover, CEM
25 Corporation, Mathews, NC, USA) equipped with a magnetic stirrer and air cooling system.
26 After the reaction the catalyst was filtered off, washed, and dried. The reusability of the lignin
27 catalyst was conducted by the same procedure with the recycled catalyst. For the comparison,
28 the separate sets of reactions under the same conditions were made in the absence of catalyst
29 and also in the presence of 5 wt% Amberlyst 15 and *p*-toluenesulfonic acid (PTSA) catalysts.
30 The final reaction mixture was carefully separated from heterogeneous catalyst and methanol
31 was separated by evaporation. Finally, the products were washed with water to remove the
32 unreacted fatty acid residues and dissolved PTSA.
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44 45 **2.2.5 Analysis of methyl esters** 46

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48 Quantitative analysis of the FAMEs produced was performed by a GC
49 Shimadzu GC-2010 (Chiyoda-ku, Tokyo, Japan) equipped with FID. A capillary column ZB-
50 Wax (30 m x 0.25 mm i.d., film thickness 0.25 µm) was used to separate the methyl esters.
51 Hexane and methyl heptadecanoate were used as solvent and internal standard (the relative
52 mass-based response used factors were equal to 1), respectively. The sample of FAMEs (2
53 mg/mL) mixed with the internal standard (1 mg/mL) in hexane was injected into GC/FID.
54 The GC oven temperature program was 2 min at 100 °C, 6 °C/min to reach 250 °C, and hold
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for 15 min, creating a total run time of approximately 42 min. The injection port had a temperature of 250 °C and the temperature of FID was 250 °C, with hydrogen and air flows at 40.0 mL/min and 400 mL/min, respectively. The results were handled with a Shimadzu LabSolutions (GCsolution, Release 2.3.1) chromatograph data system.

3 Results and discussion

The density of functional acid groups in the lignin catalyst was determined by different base titrations (Table 1). The density of $-\text{SO}_3\text{H}$ groups in the lignin catalyst was observed to be clearly lower than that in the commercial ion exchange resin Amberlyst 15 catalyst. However, the total acidity of the lignin catalyst was about 3.1 mmol/g and it almost accounted for 73 % of that of Amberlyst 15. The total acid density of the recycled lignin catalyst was reduced by 15 % compared to that of the fresh catalyst. The FT-IR spectrum of the lignin catalyst (Figure S2) showed the vibration bands at 1030 cm^{-1} (SO_3 stretching) and 1149 cm^{-1} (S-O-S stretching in $-\text{SO}_3\text{H}$) indicating the presence of $-\text{SO}_3\text{H}$ groups.²⁰ The observed vibration bands at 1557 cm^{-1} and 1698 cm^{-1} were probably the plane deformation -OH and the C=O stretching of $-\text{CO}_2\text{H}$ groups, respectively.²¹

Table 1 Density of acid groups in the catalysts (mmol/g)

| Sample | $-\text{SO}_3\text{H}$ | $-\text{CO}_2\text{H}$ | $-\text{OH}$ |
|--------------------------|------------------------|------------------------|--------------|
| Lignin catalyst | 1.4 ± 0.2 | 0.9 ± 0.2 | 0.8 ± 0.1 |
| Recycled lignin catalyst | 1.2 ± 0.2 | 0.7 ± 0.1 | 0.7 ± 0.1 |
| Amberlyst 15 | 4.2 ± 0.1 | - | - |

The elemental analysis of lignin catalyst showed the presence of sulfur (from $-\text{SO}_3\text{H}$) along carbon and oxygen (Table 2). As increase in the carbon content (due to the presence of fatty acid impurities), sulfur content in the recycled catalyst was reduced by 25 % compared to that of the fresh catalyst. There was no difference observed between the particle size of the initial lignin catalyst and recycled catalyst shown in Figure 1.

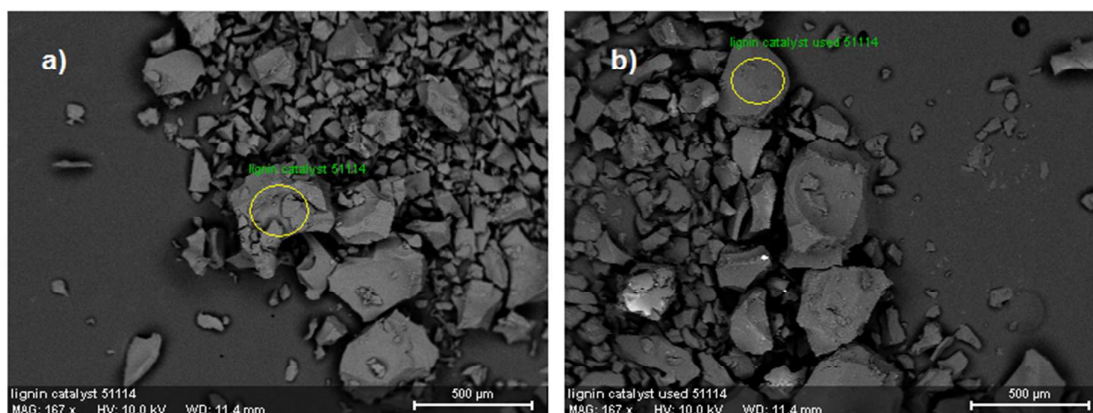


Figure 1 SEM micrographs of a) lignin catalyst and b) recycled lignin catalyst.

Table 2 Elemental analysis of the lignin catalysts (wt%)

| Sample | C | O | S |
|----------|----------|----------|---------|
| Initial | 57.7±4.8 | 38.6±3.2 | 3.7±0.4 |
| Recycled | 66.4±5.3 | 30.8±4.0 | 2.8±0.1 |

The composition of various fatty acids and resin acids in the fraction of TOFAs is presented in Figure 2. The main fatty acid components were linoleic ($C_{18:2}$), oleic ($C_{18:1}$), and linolenic ($C_{18:3}$) acids that corresponded to about 49 %, 27 %, 9 % of the total fatty acids, respectively.

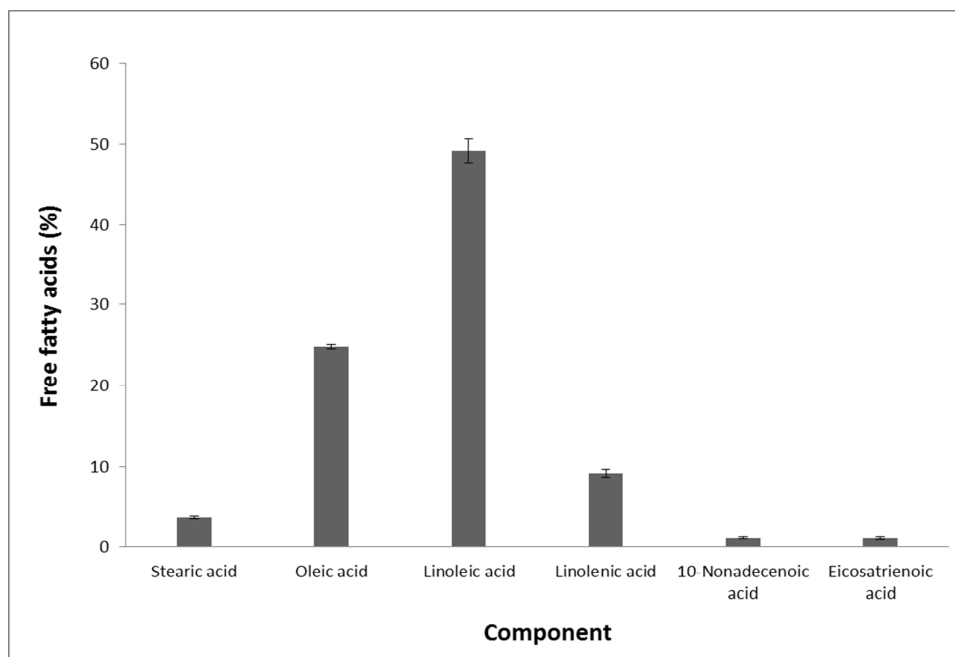


Figure 2 Weight percentages of fatty acids in the TOFAs product containing 92.4 % fatty acids, 3.2 % resin acids, and 4.4 % miscellaneous compounds.

The acid properties of the lignin catalyst material were tested for the microwave-assisted esterification of TOFAs with methanol. The reactions were carried out at different time intervals under the same conditions. Additionally, the activity and reusability of the lignin catalyst were compared under the same conditions to those of different catalytic (with Amberlyst 15 and PTSA) and non-catalytic reactions. The microwave esterification at a low methanol to fatty acids ratio showed a good yield for the catalytic reactions compared to that of the non-catalytic one. The lignin catalyst resulted almost in a FAMEs yield of 88 % which was slightly higher than that (80 %) obtained with the Amberlyst 15 catalyst (Figure 3). The maximum yield of 93 % was achieved with the homogeneous PTSA catalyst and the lowest one (20 %) by the non-catalytic reaction for 60 min. It should be pointed out that with the lignin catalyst, a FAMEs yield of about 67 % and 76 % could be obtained within a short reaction time of 10 min and 30 min, respectively.

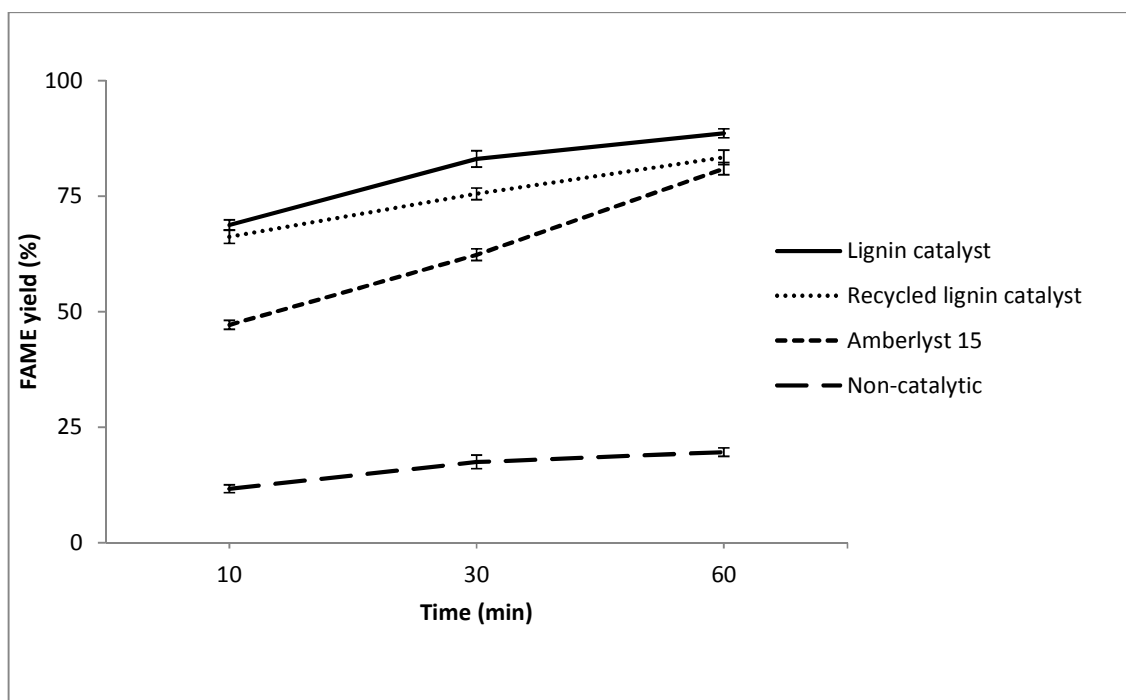


Figure 3 Esterification yields of fatty acids with methanol at various reaction times, at 100 °C, and with heterogeneous catalytic and non-catalytic reaction.

The esterification yields of the individual fatty acids varied. The TOFAs studied mainly consisted of unsaturated fatty acids; approximately about 83 % of the total compounds. The oleic acid (a monoenoic acid) and linoleic acid (a dienoic acid) showed a higher FAME yield of approximately 85 % compared to that of linolenic acid (a trienoic acid) corresponding to a FAME yield of approximately 60 % with heterogeneous catalyst for 60 min (Figure 4). The

crude FAMEs produced using lignin-based acid catalyst might contain unreacted fatty acids and resin acids along with some minimal amount of sulfur (sulfonyl acid groups) from catalyst leaching. The reusability of the lignin acid catalyst was also tested; the results suggested no significant decrease in the activity. The proper activation of lignin catalyst may further increase the reusability of it for several times. One interesting further aspect in this overall approach is that even crude methanol may also be separated from the relief gases of alkaline pulping.⁹

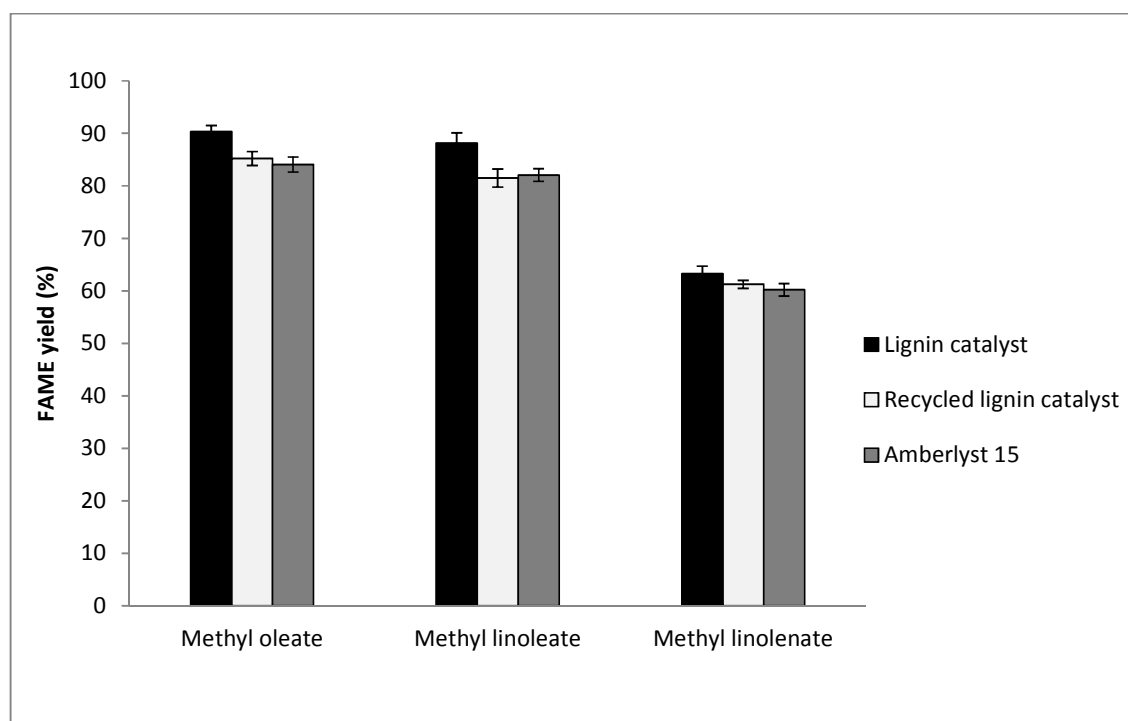


Figure 4 Esterification yields of oleic, linoleic, and linolenic acids with methanol at various reaction times, at 100 °C, and with heterogeneous catalysts.

4 Conclusions

A substantial amount of organic material, especially degraded lignin and carbohydrate-derived aliphatic carboxylic acids occurs in the black liquor from alkaline pulping. In this study, a heterogeneous catalyst containing $-\text{SO}_3\text{H}$, $-\text{CO}_2\text{H}$, and $-\text{OH}$ groups was produced from the acid-precipitated alkaline lignin by the phenol formaldehyde condensation and sulfonation reaction. This lignin catalyst exhibited high activities in the acid-catalyzed esterification of tall oil fatty acids with methanol. This is an interesting approach in the utilization of both these by-products of alkali pulping into valuable products.

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3 Compared to other catalysts (Amberlyst 15 and PTSA) tested the lignin-based catalyst
4 showed a good activity and it can also be easily recycled.
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7 8 **ASSOCIATED CONTENT**

9 10 **Supporting Information**

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14 Additional information is available free of charge on the ACS Publications website at DOI:

15
16 Production principle of tall oil fatty acid methyl esters (Figure S1) and FTIR spectra of
17 lignin catalyst (Figure S2).
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20 21 **Acknowledgement**

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24 The authors gratefully acknowledge the financial support of the Foundation for Research of
25 Natural Resources in Finland (Suomen Luonnonvarain Tutkimussäätiö).
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