Research Article

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Hydrogen-Free Deoxygenation of Bio-Oil Model Compounds over Sulfur-Free Polymer Supported Catalysts

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Abstract: Hydrotreatment of bio-oil oxygen compounds allows the final product to be effectively used as a liquid transportation fuel from biomass. Deoxygenation is considered to be one of the most promising ways for bio-oil upgrading. In the current work, we describe a novel approach for the deoxygenation of bio-oil model compounds (anisole, guaiacol) using supercritical fluids as both the solvent and hydrogen-donors. We estimated the possibility of the use of complex solvent consisting of non-polar n-hexane with low critical points ($T_c = 234.5$ ${}^{\circ}$ C, P_c = 3.02 MPa) and propanol-2 used as H-donor. The experiments were performed without catalysts and in the presence of noble and transition metals hydrothermally deposited on the polymeric matrix of hypercrosslinked polystyrene (HPS). The experiments showed that the presence of 20 vol. % of propanol-2 in n-hexane results in the highest (up to 99%) conversion of model compounds. When the process was carried out without a catalyst, phenols were found to be a major product yielding up to 95 %. The use of Pd- and Co-containing catalyst yielded 90 % of aromatic compounds (benzene and toluene) while in the presence of Ru and Ni cyclohexane and methylcyclohexane (up to 98 %) were the main products.

Keywords: bio-oil; anisole; guaiacol; deoxygenation; supercritical conditions; hypercrosslinked polystyrene; hydrothermal synthesis; aromatics; cyclohexanes.

1 Introduction

The fast depletion of fossil fuel resources as well as the high value of green-house-gas emissions leads to the development of novel ways for the production of energy and chemicals [1]. Biomass is considered to be one of the most permissive sources for transportation fuels and chemicals as it contains a variety of compounds and is characterized by a high energy content [2]. In spite of numerous ways to process the biomass, they are limited by the variety and complexity of the biomass composition and structure. Fast pyrolysis is considered to be one of the most promising methods, allowing the lignocellulosic biomass to be effectively converted into the liquid called bio-oil [3-6]. However, the complex composition of bio-oil makes the fast pyrolysis product inappropriate for direct use as fuel [7]. As far as the bio-oil is presented by the phenolic compounds formed during the depolymerization of lignin, high oxygen content and high acidity lead to such disadvantages as pure storage stability, low heating value, high viscosity, and low lubricity [8-11]. Because of this, the bio-oil needs to be upgraded through a decrease in the oxygen compound concentration (e.g. through deoxygenation).

The upgrading of bio-oil can be performed by either zeolite catalyzed cracking [12-14] or hydrodeoxygenation/ hydrogenation in the presence of transition and noble metal catalysts [15-19]. The first process seems to be ineffective due to the low quality of the final product [14]. Thus, the hydrodeoxygenation is considered to be the most optimal way for bio-oil upgrading. The pioneering work on the bio-oil hydrodeoxygenation was published by D.C. Elliott at al. [20]. The authors used the common

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hydrodesulfurization NiMo and CoMo catalysts which are widely applied for deoxygenation. However, such catalysts showed low effectiveness due to the fast coke formation. For this reason, the researchers focused on the use of noble metals (Ru, Pd, Pt, Re) to remove oxygen from bio-oil [21-35].

There are numerous works devoted to the hydrodeoxygenation of either bio-oil or the bio-oil model compounds. Almost all studies are carried out in a hydrogen atmosphere in the medium of C_{10} - C_{14} hydrocarbons as a solvent [15, 21, 26-35]. This leads to the formation of phenols and cyclic alcohols as a major product. While using some catalysts (e.g. noble metals supported on the activated carbon or carbon nanotubes), aromatic and cyclic compounds can be produced [15, 21, 36-40] Due to the high viscosity of the solvents used as well as the low hydrogen solubility, the process requires harsh conditions (temperature and pressure) to be used. Typically, the hydrodeoxygenation is performed at a temperature of 300-400 $^{\circ}$ C and a pressure of 1.0-2.0 MPa.

The recent tendencies in deoxygenation focus on the process conduction using hydrogen-free approaches. For these techniques, supercritical fluids are used. Supercritical water is one of such promising solvents, which allows the process to be carried out either without catalysts or in the presence of transition metal catalysts. The first way (without catalysts) results in the formation of phenols (phenol, catechol, cresol). The last one (with catalysts) allows aromatics to be obtained [27-35]. Among the other solvents used are tetraline [41-43], methanol [44-46], ethanol [47, 48], secondary alcohols [49-51] and formic acid [25]. The last two compounds are used as hydrogen-donors. In the presence of noble metal catalysts, tetralin, methanol, and formic acid lead to the formation of aromatics and cyclohexanols, while ethanol and secondary alcohols result in alkylphenols production [47-51].

In the current work, we describe the conversion of model bio-oil compounds (guaiacol and anisole) in a hydrogen-free atmosphere in the medium of supercritical hexane and in the complex (hexane:alcohol) supercritical solvent in the presence of polymer-supported catalysts synthesized by the hydrothermal deposition of noble and transition metals in the polymeric matrix of hypercrosslinked polystyrene.

2 Experimental

2.1 Materials

Anisole (99%, Acros Organics, Belgium) and guaiacol (99 %, Acros Organics, Belgium) were used as bio-oil model compounds without preliminary purification. n-Hexane (CG, Reachim, Russia) and propanol-2 (CG, Reachim, Russia) were used as solvents. Non-functionalized hypercrosslinked polystyrene (HPS, MN270, Purolight Ltd., UK) was chosen as catalyst support due to its high surface area, thermal stability and chemical inertness [52, 53]. Palladium chloride (99 %, Sigma Aldrich, USA), ruthenium (IV) hydroxochloride (99 %, Aurat, Russia), nickel nitrate (99 %, Reachim, Russia), cobalt nitrate (99 %, Reachim, Russia) were used as metal precursors for catalyst synthesis. The catalysts with the metal content 5 wt. % were synthesized by the hydrothermal deposition according to the procedure described in [54]. The synthesized catalysts were reduced in a hydrogen flow at 300 °C for 5 hours before the experiments.

2.2 Deoxygenation procedure

Deoxygenation experiments were performed in a six-cell reactor Parr Series 5000 Multiple Reactor System (Parr Instrument, USA) equipped with a magnetic stirrer. In a typical experiment, 1 g of the bio-oil model compound was dissolved in 30 mL of solvent. The mixture was put into the reactor cell and 0.05 g of the catalyst was added. The reactor was sealed and purged with nitrogen three times in order to remove air. Then the nitrogen pressure was set at 3.0 MPa, and the reactor was heated up to 270 °C. After the reaching of the reaction temperature, the pressure increased up to 6.8-8.5 MPa depending on the solvent composition. The solvent composition varied from 0 to 30 vol. % of propanol-2 in n-hexane. In order to exclude the equilibrium shift, the process was performed for varying times - from 10 to 90 min with a 10 min interval.

The liquid phase was analyzed by GCMS using a gas chromatograph GC-2010 and mass-spectrometer GCMS-QP2010S (SHIMADZU, Japan) equipped with a chromatographic column HP-1MS with 30 m length, 0.25 mm diameter and 0.25 μ m film thickness. The column temperature program was set as follows: initial temperature 120 °C was maintained for 5 min then the column was heated up to 250 °C with the rate of 5 °C/min and maintained at 250 °C for 5 min. Helium (volumetric velocity of 20.8 cm³/s, the pressure of 253.5 kPa) was used

as a gas-carrier. The injector temperature was 280 °C, ion source temperature was 260 °C; interface temperature – 280 °C.

The quantitative estimation of the deoxygenation process was performed using the relative reaction rate, substrate conversion and product yield calculated according to the Equations 1-3. The calculations were performed on the basis of the reaction mass-balance (Eq. 4).

$$X = \frac{C_0 - C}{C_0} \cdot 100\%$$
 (1)

$$W = \frac{C_0 \cdot X}{\tau} \tag{2}$$

$$Y = \frac{C_i}{\Sigma C_i} \cdot X \tag{3}$$

where X – substrate conversion, C_0 – initial substrate concentration, C – current substrate concentration, W – relative reaction rate, τ – reaction time, Y – product yield, Ci – product concentration.

$$m_{0BOC} = \sum_{i=1}^{n} m_{iPH} + \sum_{i=1}^{n} m_{iAR} + \sum_{i=1}^{n} m_{iCYC} + m_{rBOC}$$
(4)

where $m_{0 BOC}^{}$ – an initial mass of the bio-oil model compound, $m_{i PH}^{}$ – a mass of phenolic compounds, $m_{i}^{}$ – a mass of aromatic compounds, $m_{i CYC}^{}$ – a mass of cyclic compounds, $m_{r BOC}^{}$ – a residual mass of the bio-oil model compound. Masses were calculated on the basis of concentrations obtained during the chromatogram analysis.

3 Results and discussion

3.1 Influence of the solvent composition

The influence of the solvent composition on the deoxygenation of the bio-oil model compound was studied without the catalyst. The solvent composition varied from 0 to 30 vol. % of propanol-2 in n-hexane. The results of the experiments are presented in Figures 1 and 2, and in Table 1. While analyzing the kinetic curves it is obvious that the curve slope is similar for all cases which can indicate the close reaction rates as well as the similar conversion



Figure 1: Influence of propanol-2 concentration on anisole conversion.



Figure 2: Influence of propanol-2 concentration on guaiacol conversion.

mechanism. The calculation of the relative reaction rates at 50% of substrate conversion (according to Equation 2) showed that the values obtained seem to be close to each other. Thus, the solvent composition practically does not affect the rates of bio-oil model compound conversion.

In spite of the solvent, the composition does not practically influence the reaction rate, the product composition strongly depends on the propanol-2 concentration. The analysis of the reaction products showed the preferred formation of the phenolic compounds (phenol and pyrocatechol) indicating the ether bond hydrolysis during the reaction (Fig. 3, 4) [55]. Methanol was also observed among the reaction products confirming the proposed reaction route. A negligible amount of aromatics (mainly benzene) were also obtained. When the propanol-2 concentration was lower than

Propanol-2 concentration, vol. %	Relative rate of conversion at 50 % of conversion, mol·L ⁻¹ ·min ⁻¹		Phenol yield, %		Aromatic yield, %	5
	Anisole	Guaiacol	Anisole	Guaiacol	Anisole	Guaiacol
0	0.0035	0.0028	69	65	2	1
10	0.0037	0.0030	78	73	4	2
20	0.0045	0.0034	94	91	5	7
30	0.0039	0.0032	95	91	3	1



Figure 3: Kinetic curves for non-catalytic deoxygenation of anisole.



Figure 4: Kinetic curves for non-catalytic deoxygenation of guaiacol.

20 vol. %, the phenolic compound yield did not exceed 78 % probably due to the low concentration of H-donor. The highest phenol yield (up to 94 %) was observed at a propanol-2 concentration of 20 vol. %. The increase in the propanol-2 concentration did not lead to an increase in the phenol yield. Thus, based on the results obtained, the solvent composition of 80 vol. % of n-hexane and 20 vol. % of propanol-2 was chosen for further experiments.

Figure 5: Kinetic curves for the deoxygenation of anisole in the presence of 5%-Co-HPS.

3.2 Influence of the catalysts

The use of the catalysts synthesized by hydrothermal deposition leads to a significant increase in the rate of bio-oil model compounds conversion (see Table 2). The highest conversion rate for both anisole and guaiacol was observed while using Ni- and Pd- containing catalysts. Co- and Ru-based catalysts showed a lower deoxygenation rate due to the lower catalytic activity of the metals in the heteroatom removal [33, 34].

The analysis of the reaction products showed that the presence of 5%-Pd-HPS and 5%-Co-HPS resulted in the formation of up to 90 % of aromatic compounds (benzene and toluene) indicating the behavior of deoxygenation and transmethylation reactions [55]. It should be noted that while using Pd- and Co-containing catalysts, phenol, and pyrocatechol were observed in the reaction mixture (Fig. 5, 6). These results correlate well with the literature data for palladium and cobalt catalysts [18, 26, 30, 34, 36, 51]. Meanwhile, the use of 5%-Ru-HPS and 5%-Ni-HPS led to the formation of 99 % of cyclic compounds (cyclohexane and methylcyclohexane). In this case, transmethylation and hydrogenation were the main reaction routs [55].



Catalyst	atalyst Relative rate of conversion % of conversion, mol·L ⁻¹ ·mi		0 Phenol yield, %		Aromatic yield, %		Cyclic compound yield, %	
	Anisole	Guaiacol	Anisole	Guaiacol	Anisole	Guaiacol	Anisole	Guaiacol
Non-catalytic	0.0045	0.0034	94	91	5	7	-	-
5%-Co-HPS	0.0064	0.0046	9	15	87	83	4	2
5%-Ni-HPS	0.0096	0.0077	-	-	1	2	99	98
5%-Pd-HPS	0.0086	0.0066	3	6	91	90	6	4
5%-Ru-HPS	0.0072	0.0055	-	-	3	5	97	95

Table 2: Catalyst influence on bio-oil model compound conversion.



Figure 6: Kinetic curves for the deoxygenation of guaiacol in the presence of 5%-Co-HPS.



Figure 7: Kinetic curves for the deoxygenation of anisole in the presence of 5%-Ni-HPS.

Moreover, a trace amount of cyclohexanol (up to 0.5 %) was formed in the presence of these catalysts (Fig. 7, 8). The formation of cycloalkanes can be explained by the high hydrogenating activity of Ru and Ni [26, 28, 29, 32,



Figure 8: Kinetic curves for the deoxygenation of guaiacol in the presence of 5%-Ni-HPS.

34, 49, 50]. Cobalt did not exhibit hydrogenating activity probably due to the lower degree of the reduction of the active metal (see Fig. 1S) [56, 57].

Based on the deoxygenation product analysis, the following schemes of anisole and guaiacol conversion in the presence of hydrothermally synthesized catalysts can be proposed (Figures 9 and 10). Thus, the synthesized catalysts can be effectively applied in the bio-oil upgrading in the medium of supercritical complex solvent resulting in over 85 % of oxygen removal for 70 minutes.

4 Conclusions

The conversion of model bio-oil compounds in a hydrogen-free atmosphere in the medium of supercritical and in a complex supercritical solvent was studied in the presence of polymer-supported catalysts synthesized by the hydrothermal deposition on the polymeric matrix of HPS. The study of the solvent composition's influence on the anisole and guaiacol deoxygenation showed that



Figure 9: Possible scheme of anisole conversion (half arrow – in the non-catalytic process; solid arrows – in the presence of 5%-Pd-HPS and 5%-Co-HPS; dash arrows – in the presence of 5%-Ru-HPS or 5%-Ni-HPS).



Figure 10: Possible scheme of guaiacol conversion (half arrow – in the non-catalytic process; solid arrows – in the presence of 5%-Pd-HPS and 5%-Co-HPS; dash arrows – in the presence of 5%-Ru-HPS or 5%-Ni-HPS).

the solvent consisting of 80 vol. % of n-hexane and 20 vol. % of propanol-2 was optimally providing up to 98 % of substrate conversion. The bio-oil model compound processing without a catalyst results in the formation of phenolic compounds, while the use of 5%-Pd-HPS or 5%-Co-HPS and 5%-Ru-HPS or 5%-Ni-HPS provides the formation of aromatic and cyclic compounds respectively. The synthesized catalysts result in over 85 % of oxygen removal from bio-oil for 70 minutes.

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