

Article

Hydrogenation of Bio-Oil Model Compounds over Raney-Ni at Ambient Pressure

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Abstract: Lignocellulosic biofuels are the most promising sustainable fuels that can be added to the crude oil pool to refill the dwindling fossil resources. In this work, we tested a Raney-Ni catalyst for the hydrogenation of four bio-oil model compounds and their binary mixtures to assess their reactivity under mild conditions suitable for bio-oil stabilization preceding green diesel production from lignocellulosic biomass. The hydrogenation experiments were performed at ambient hydrogen pressure at temperatures in the range 30–70 °C. Raney-Ni was found to hydrogenate all investigated model compounds efficiently; both carbonyl groups and double bonds were saturated. In addition, it was also active in the demethoxylation of guaiacol. When studying the binary mixtures, furfuryl alcohol was found to significantly inhibit the hydrogenation of the other model compounds (guaiacol and methyl isobutyl ketone) due to their very strong adsorption.

Keywords: Raney-Ni; bio-oil; model compounds; hydrogenation; green diesel

1. Introduction

Green diesel production has been developing rapidly over the past decade, and the annual capacity of the commercial units has exceeded 2 million tons thanks to the NexBTL and Ecofining technologies [1,2]. Both technologies use vegetable oils and animal fats (including waste oils and fats) as feedstock, which presents a significant limitation for their further growth due to the restricted availability of these feedstocks. While microbial or algal oils can be considered as feedstocks of the future, lignocellulosic biomass continues to be the most abundant and available among biomass resources. Therefore, lignocellulosic biomass has attracted interest as a sustainable resource for the production of high-quality biofuels with high energy density relying on a wide variability of non-food feedstocks (e.g., straw, wood, miscanthus, rice husks) [3].

Fast pyrolysis is one of the thermochemical conversion technologies of lignocellulosic biomass. It affords a liquid biofuel intermediate called bio-oil [4]. Bio-oil is a viscose, corrosive dark liquid containing a high amount of water, and is immiscible with petroleum fractions. Thus, it has to be upgraded to become a petroleum-compatible feedstock. Catalytic hydrogenation over a wide range of metallic catalysts (e.g., sulphided, transition, and noble metals) has great potential for upgrading and refining bio-oil to produce high-quality and cost-competitive substitutes of petroleum fuels [5–7]. To achieve the desired product quality, hydrogenation is usually performed under severe reaction conditions (200–400 °C, 1–29 MPa) [8,9]. According to Lei et al. [10], bio-oil contains mainly phenols, aliphatic hydrocarbons, aromatic hydrocarbons, furan derivatives, and some acids. Phenols and guaiacols make up about 28%–40% of bio-oils, depending on the reaction conditions, and consist of phenols, methyl phenols, ethyl phenols, and methoxy phenols [10]. Phenols are produced through the cleavage of ether (mainly α or β -o-4 bonds) and CC linkages during the pyrolysis of lignin. Lignin sources are becoming more abundant with the development of the lignocellulose-to-ethanol

industry [11]. However, the main use of lignin is as a low-grade energy source in combustion. However, Huber et al. [12] and Holladay et al. [13] pointed out that the overall revenue could be improved from \$12 to \$35 billion if lignin was used to produce chemicals and transportation biofuels (green fuels) rather than low-grade energy. As an alternative, pyrolytic lignin has attracted interest as a renewable resin due to its good compatibility with phenol formaldehyde resin formulations. This interest is enhanced by the fact that high lignin content biomass is widely available, often at low cost and in large quantities, while phenol is a relatively expensive bulk chemical that is manufactured from increasingly costly crude oil [14].

Despite the attention that bio-oil upgrading has attracted and its potential to yield green diesel fuel components (i.e., to yield hydrocarbons in the diesel fuel range), a fundamental understanding of mutual inhibition or promotion effects among the compounds present in real bio-oils is lacking, which hampers the development of more efficient bio-oil upgrading catalysts.

It is well-documented that bio-oil consists of hundreds of different organic molecules with different upgrading chemistry including, for example, hydrogenation, deoxygenation, hydrogenolysis, decarboxylation, and dehydration reactions [15]. The identification and quantification of the individual compounds in both raw bio-oils and the upgraded products is very challenging. While most of these compounds can be assigned to different groups (e.g., phenols, ketones, aldehydes, acids, or alcohols) based on their functional groups, this might not be sufficient for describing their reactivity in upgrading by hydrotreatment [16,17].

Therefore, many researchers have used different model compounds to study hydrogenation catalysts for bio-oil upgrading and to understand and describe the reaction routes of each compound in order to assess the potential of these catalysts in bio-oil hydrogenation [18,19]. Among the wide variety of hydrogenation catalysts, Raney nickel catalysts stand out due to their very high catalytic activity under mild reaction conditions. This is advantageous for stabilizing bio-oil that undergoes undesired condensation reactions at elevated temperatures, resulting in fast catalyst deactivation.

Raney-Ni is a well-known heterogeneous catalyst used in industrial organic syntheses, such as in the hydrogenation of dextrose to sorbitol and benzene to cyclohexane [20,21]. More importantly, from the bio-oil upgrading point of view, Raney-Ni was successfully applied in the in-situ hydrogenation of model compounds in methanol–water solutions in batch reactors [22]. This method does not need an external hydrogen source because hydrogen for the reaction is produced from the solvent by aqueous phase reforming (APR) that makes this process more economically feasible [23,24]. According to Feng et al. [25] who studied hydrogenation of guaiacol, the addition of methanol to the reaction mixture, together with increased reaction temperature, led to a significantly increased guaiacol conversion (from 65% at 120 °C and pressure 3 MPa to 98% at 240 °C). There was a substantial rise in the conversion of methanol (from 23% to 70%) and selectivity for hydrogen production when the reaction temperature was increased from 160 °C to 240 °C. The recyclability of Raney-Ni was verified in three subsequent catalytic tests. The conversion of guaiacol decreased to 75% over the three-times reused catalyst from 98% obtained over the fresh catalyst. Similarly, Xu et al. [23] reported the importance of the increase in the reaction temperature for both the hydrogenation of acetone to isopropanol or phenol to cyclohexanol and the reforming of methanol. According to Bai [26], the activity of Raney-Ni depends on hydrogen pressure and decreases with the increasing pressure. In addition to the model compounds, Xu also studied the in-situ hydrogenation of bio-oil and reported that the content of ketone/aldehyde and organic acids decreased, while the content of phenols did not change significantly during hydrogenation. Moreover, esterification took place during the upgrading process. On the other hand, the content of alcohols and esters increased dramatically due to the hydrogenation of ketones/aldehydes and the esterification of organic acids by alcohols. Most of the studies using bio-oil model compounds were performed mainly in the presence of methanol as a hydrogen source at temperatures above 150 °C. However, milder reaction conditions and possible inhibition effects during hydrogenation of at least two model compounds have been studied only scarcely, if at all [27].

Nonetheless, an understanding of these effects is crucial for developing an optimal reaction system for bio-oil upgrading into green diesel fuel components.

A major challenge in the hydrogenation of different model oxygenates to produce green diesel components are high reaction temperatures and high hydrogen pressure to maintain the catalysts activity and to achieve desired yields. Morais et al. [28] successfully hydrogenated cattle fat at a reduced hydrogen pressure (i.e., 5.5 bar) in the presence of supercritical CO₂ (total pressure CO₂ + H₂ of up to 140 bar) using an industrial heterogeneous catalyst in a batch reactor. The 64% yield of saturated hydrocarbons (after 2 h at 5.5 bar H₂) was increased to 75% when H₂ with supercritical CO₂ was used. By extending the reaction the time to 6 h, a further increase in the yield to 90% was achieved. However, at the same time the acid number of this product increased from the 5.65 mg_{KOH}/g for the feed to 23 mg_{KOH}/g.

Hydrogenation (including defunctionalization and hydrodeoxygenation) of bio-oil model compounds (32 model compounds) dissolved in propan-2-ol was also studied extensively by Wang et al. [29] over Raney-Ni 2800 using a large excess of catalysts (the catalyst-to-feed ratio was 5:1). Propan-2-ol acted not only as solvent, but also as an H-donor due to the cleavage of the O–H and α -C–H bonds after adsorption onto the Ni surface. As a result, two H atoms remained adsorbed while acetone was released from the Ni surface. In addition, Raney-Ni and other Ni catalysts were reported to catalyze the transfer hydrogenation of ketones, phenols, aldehydes, and other molecules [30,31]. Wang et al. [29] also demonstrated a good recyclability of the Raney-Ni catalyst in five consecutive phenol hydrogenation experiments. Although the transfer hydrogenation of phenol using propan-2-ol was reported to require ca. 10 times more Raney-Ni catalyst than the conventional hydrogenation with H₂ [32], the good recyclability and selectivity of Raney-Ni eliminated this economical issue and would thus make the overall process more economical due to the use of milder reaction conditions.

Therefore, we studied and herein present the results of the hydrogenation of single bio-oil model compounds (i.e., guaiacol, furfural, furfuryl alcohol, methyl isobutyl ketone) and their mixtures over a Raney nickel catalyst at 30–70 °C and ambient hydrogen pressure. Guaiacol was chosen as a typical representative of the lignin decomposition products, which are predominantly aromatic phenolic compounds with methoxy functional group. Furfural (FF) and furfuryl alcohol (FFOH) were chosen to represent the products of cellulose decomposition and dehydration, which are typically furanic compounds with an aldehyde functional group that can be readily hydrogenated to a respective alcohol functional group. Finally, methyl isobutyl ketone (MIBK) was selected as a representative of the ketones present in bio-oils.

2. Results and Discussion

In the first part, we discuss and compare the results of single model compounds hydrogenation tests. In the second part, we present the results of the hydrogenation tests using model compound mixtures to explore the possible inhibition or promotion effects of different functional groups.

2.1. Single Compounds Hydrogenation

2.1.1. Guaiacol

Guaiacol hydrogenation was carried out at 30, 50, and 70 °C, ambient pressure, and feed-to-catalyst ratio 1, and its results are presented in Figure 1. Fairly high conversion (>70%) was obtained at as low a temperature as 70 °C in an 8-h experiment (Figure 1a), whereas at 30 °C only <5% conversion was observed. Based on the guaiacol conversion as a function of the reaction temperature we calculated the activation energy for guaiacol hydrogenation (Figure 1b) to be 86.2 kJ/mol. The following four compounds were detected in the reaction products: methoxycyclohexanol, phenol, cyclohexanol, and methanol. Their yields are presented in Figure 1c–f. Based on the product distribution, it can be concluded that guaiacol underwent demethoxylation and hydrogenation, ultimately yielding cyclohexanol as the main reaction product (along with methanol), which is consistent with the results

obtained by Wang et al. [29] for the guaiacol hydrogenation, although they obtained higher guaiacol conversion (100%). Whereas we observed phenol in our products as an intermediate product between guaiacol and cyclohexanol, Wang et al. [29] found only cyclohexanol without any phenol. This reflects the more severe hydrogenation conditions used in their study. From the yields of the individual compounds, it can be inferred that demethoxylation followed by hydrogenation was the primary reaction pathway. However, it was accompanied by the parallel direct hydrogenation of guaiacol, affording methoxycyclohexanol. Experiments with different feed-to-catalyst ratios indicated that the reaction was not mass-transfer-limited, even at high catalyst loadings (Figure S1).

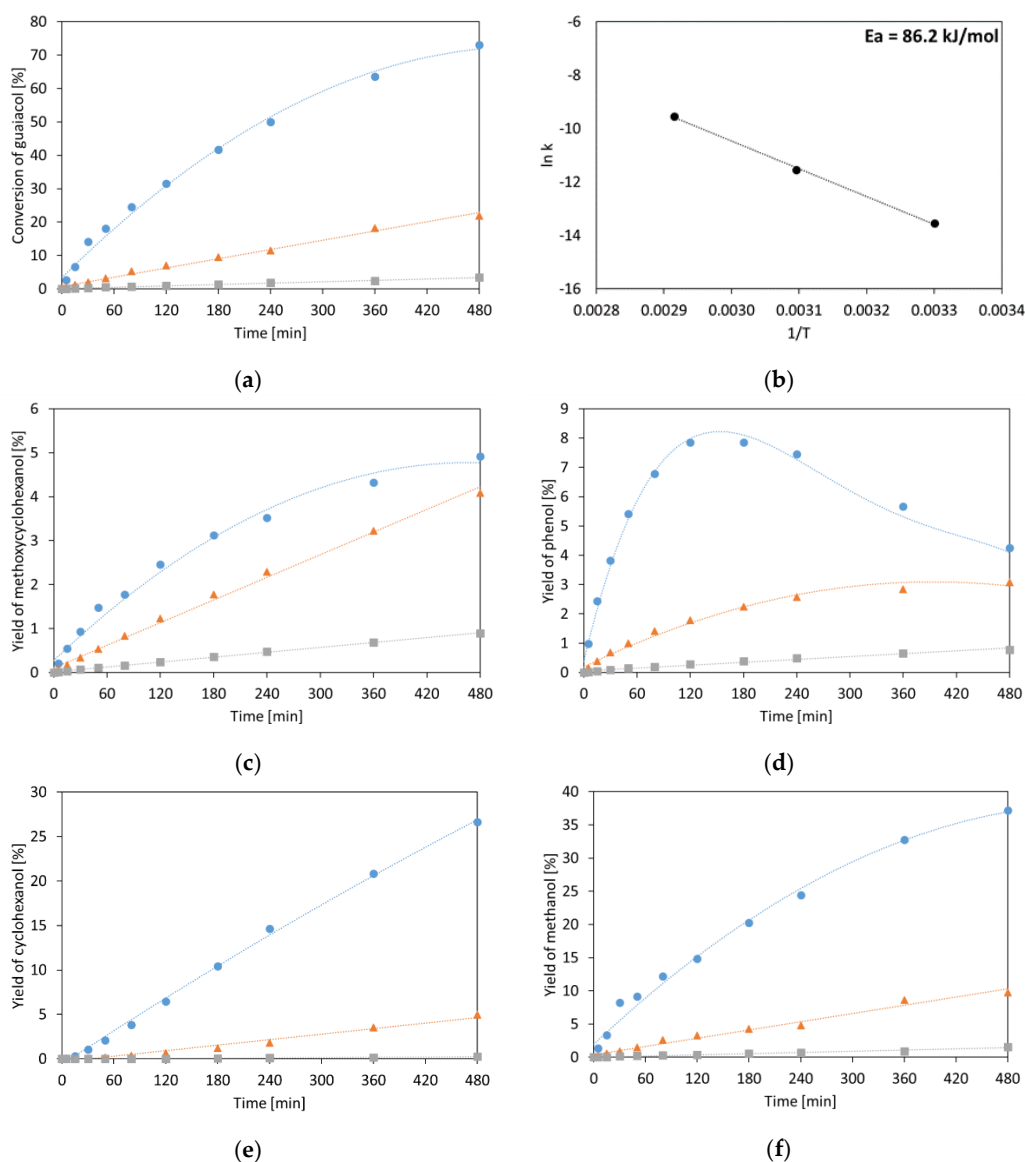


Figure 1. (a) Conversion of guaiacol, (b) Arrhenius plot. Yield of (c) methoxycyclohexanol, (d) phenol, (e) cyclohexanol, and (f) methanol at 30, 50, and 70 °C.

2.1.2. Furfural

Furfural hydrogenation tests were carried out at the same reaction conditions as for guaiacol with a feed-to-catalyst ratio of 1. However, in contrast with guaiacol, furfural conversion was virtually independent of the reaction temperature, and the calculated activation energy of furfural hydrogenation was only 2.5 kJ/mol (Figure 2b). This suggests that the apparent rate of furfural hydrogenation was governed by the adsorption of furfural or desorption of the main product (i.e.,

furfuryl alcohol). Furfuryl alcohol (FFOH) and tetrahydrofurfuryl alcohol (THFFOH) were detected as the only products in the reaction mixtures. Interestingly, FFOH yields decreased after 240 reaction minutes (i.e., after complete conversion of FF was achieved). This decline was accompanied by an increase in the THFFOH yields. This indicates that FF inhibits the subsequent hydrogenation of the primary hydrogenation product (i.e., FFOH). It is also obvious that the aldehyde group was hydrogenated rapidly. To obtain information on the subsequent hydrogenation of the furanic ring, conversion of FFOH was studied separately.

Previously, the conversion of furfural after 3 h was reported to be only 44% (at 120 °C and feed-to-catalyst ratio of 0.2) and furan was found among the products [29]. In contrast, we did not observe any C–C bond cleavage, and only FFOH and THFFOH were formed. This difference can be attributed to the lower temperature used in our study that favored selective hydrogenation without side-reactions leading not only to furan formation, but also to resin formation that could be responsible for catalyst deactivation.

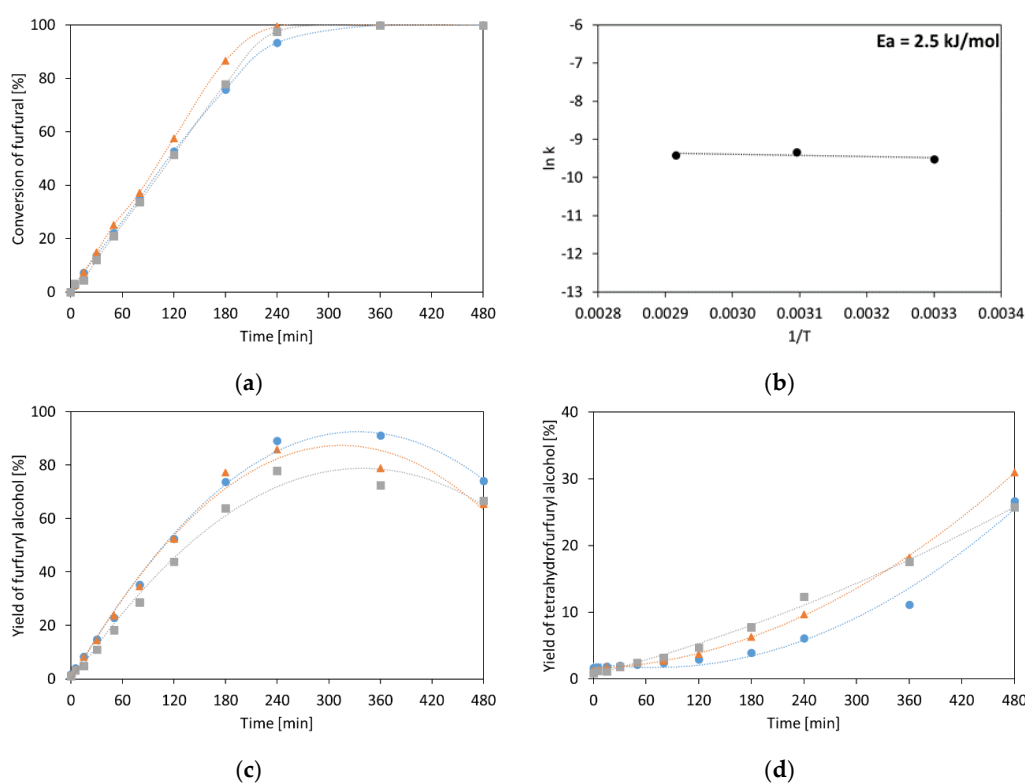


Figure 2. (a) Conversion of furfural, (b) Arrhenius plot. Yield of (c) furfuryl alcohol and (d) tetrahydrofurfuryl alcohol at 30, 50, and 70 °C.

2.1.3. Furfuryl Alcohol

Furfuryl alcohol (FFOH) was thus used as a feedstock to simulate the behavior of furfural hydrogenation products and to avoid interference by furfural (e.g., due to catalyst deactivation). The results of FFOH hydrogenation experiments at 30–70 °C with 10 °C step are presented in Figure 3. Unlike in the case of FF, a certain temperature dependence was observed over the studied temperature range (Figure 3a). Based on the experimental data, the activation energy of 16.1 kJ/mol was obtained. The low value of activation energy indicates that adsorption/desorption phenomena play an important limiting role in FFOH conversion, although not as important as in the case of FF conversion. Tetrahydrofurfuryl alcohol (THFFOH) was the main reaction product in the experimental range. The formation of dihydrofurfuryl alcohol (DHFFOH) and its yield curve as a function of temperature confirmed that FFOH hydrogenation occurred via this intermediate (Figure 3c). In addition, 1,2-pentanediol and 1,5-pentanediol were formed due to the hydrogenolysis

of the C–O bond in the furanic ring. However, the data do not unanimously prove from which furanic intermediate was formed (Figure 3e,f). Interestingly, the ratio between both alcohols was constant in the entire range of the reaction time, and this trend was valid for each reaction temperature. This implicates that they were formed from the same intermediate.

Previously, Song et al. [33] hydrogenated FFOH to THFFOH over Raney-Ni in an autoclave reactor at 110 °C and 3 MPa with 3.18 g of a Raney-Ni catalyst and 60 mL FFOH dissolved in 60 mL ethanol. The conversion of FFOH was 99.2%, with the selectivity to THFFOH being 99.9% after 90 min. This agrees well with our results, where we obtained full conversion of FFOH at 70 °C and ambient H₂ pressure after 360 min, with the selectivity to THFFOH being 90%.

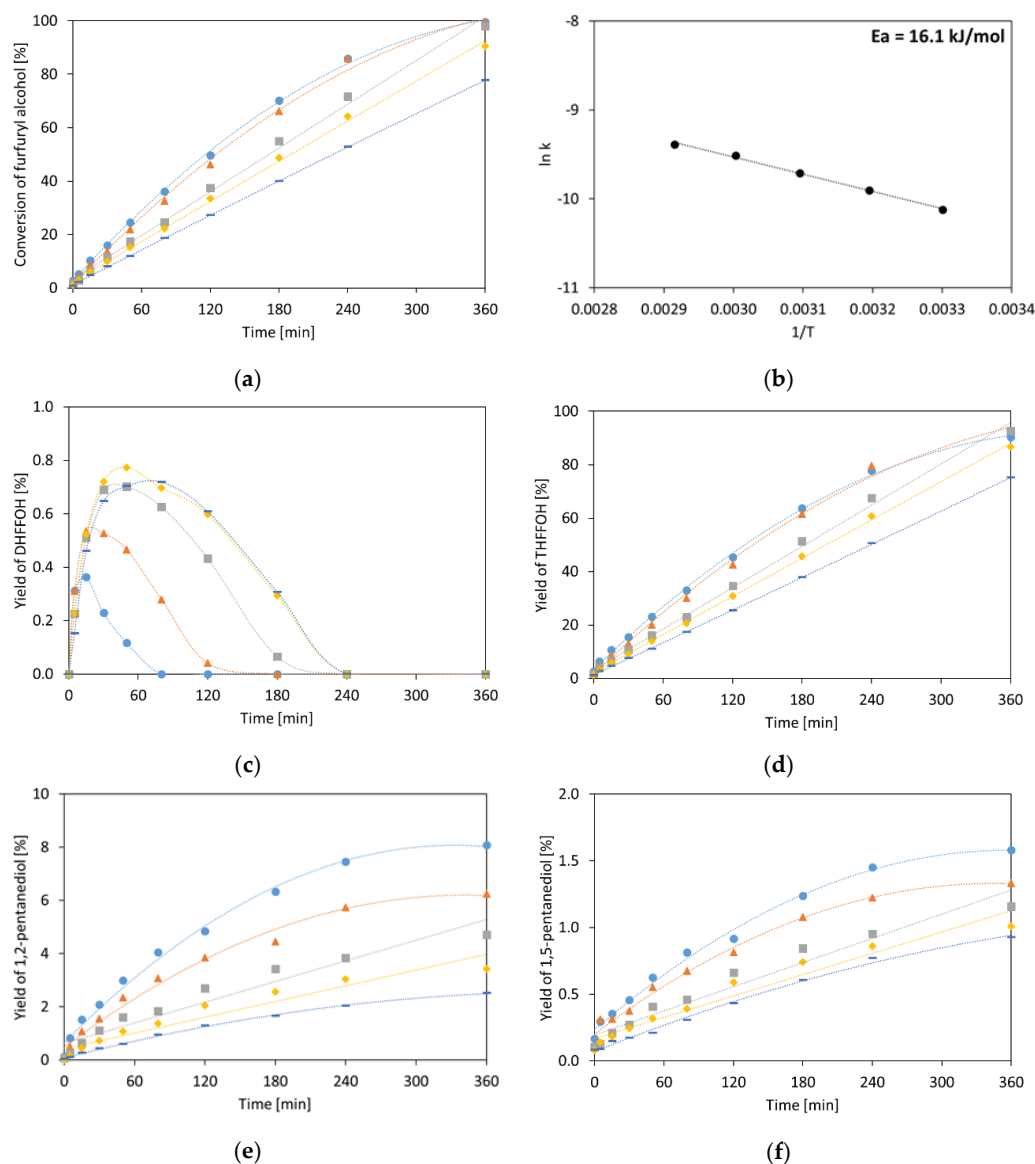


Figure 3. (a) Conversion of FFOH, (b) Arrhenius plot, Yield of (c) dihydrofurfuryl alcohol (DHFFOH), (d) tetrahydrofurfuryl alcohol (THFFOH), (e) 1,2-pentanediol, and (f) 1,5-pentanediol at 30, 40, 50, 60, and 70 °C.

2.1.4. Methyl Isobutyl Ketone

The results of MIBK hydrogenation in isopropanol are presented in Figure 4. An expected temperature dependence was observed as in the case of guaiacol, and the calculated activation energy amounted to 37.2 kJ/mol. This indicates that the reaction yielding 4-methyl-2-pentanol as the only

product was not limited by adsorption/desorption phenomena, and that it was more facile than the hydrogenation of guaiacol. Moreover, a dramatic decrease in MIBK conversion was observed when isopropanol was replaced by water (Figure 4a). This indicates limitations in hydrogenation under aqueous phase conditions. Furthermore, the experiments with MIBK as well as with the other model compounds revealed that isopropanol acted as hydrogen donor under the studied reaction conditions. We did not find any scientific papers dealing with the hydrogenation of MIBK over Raney-Ni. However, Alotaibi et al. [34] tested a wide range of hydrogenation catalysts, such as Pd/C, Pt/H-ZSM-5, Pd/SiO₂, and Cu/SiO₂, in a fixed bed reactor for the conversion of MIBK. However, these catalysts were not as efficient as Raney-Ni. The selectivity to 4-methyl-2-pentanol of 100% was achieved only over Cu/SiO₂ at 200 °C, but the conversion of MIBK was only 34% at time on stream 4 h.

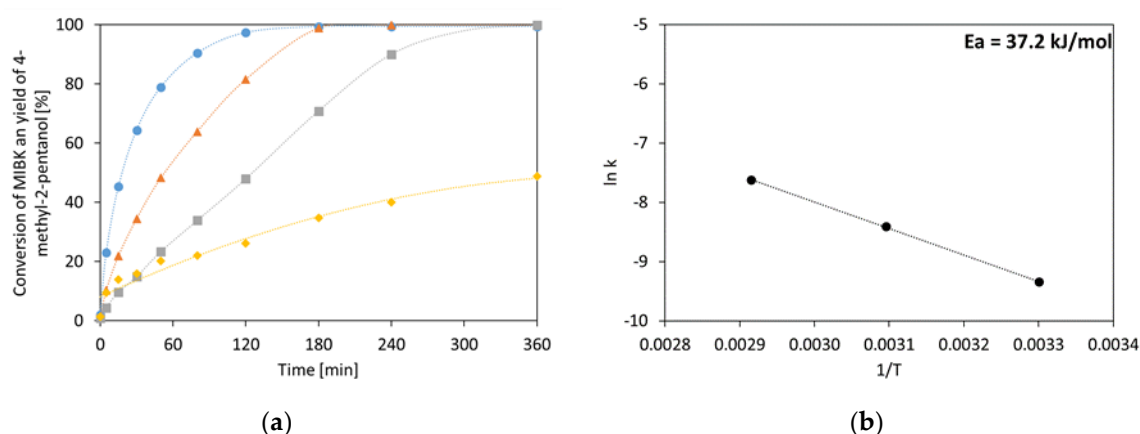


Figure 4. (a) Conversion of MIBK and yield of 4-methyl-2-pentanol and (b) Arrhenius plot for experiments at 30, 50, and 70 °C in isopropanol and water mixture at 70 °C.

2.2. Hydrogenation of Binary Mixtures

2.2.1. Guaiacol with Furfuryl Alcohol

Hydrogenation of guaiacol mixtures with FFOH (90:10, 80:20, and 50:50 mol:mol) was carried out at the same reaction conditions as for single compounds in isopropanol. Hydrogenation results are presented in Figure 5 for guaiacol, and in Figure 6 for FFOH.

Guaiacol conversion (Figure 5a) was extremely suppressed by adding even a small amount of FFOH. Interestingly, the difference in conversion values between pure guaiacol and 90:10 mixture at 360 min was 27%, but it was only 15% and 13% between 90:10–80:20 and 80:20–50:50, respectively.

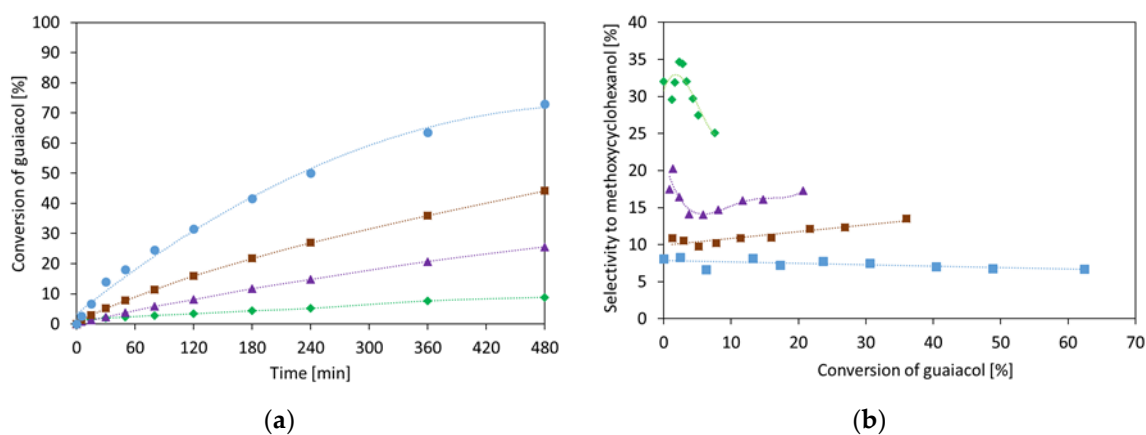


Figure 5. Cont.

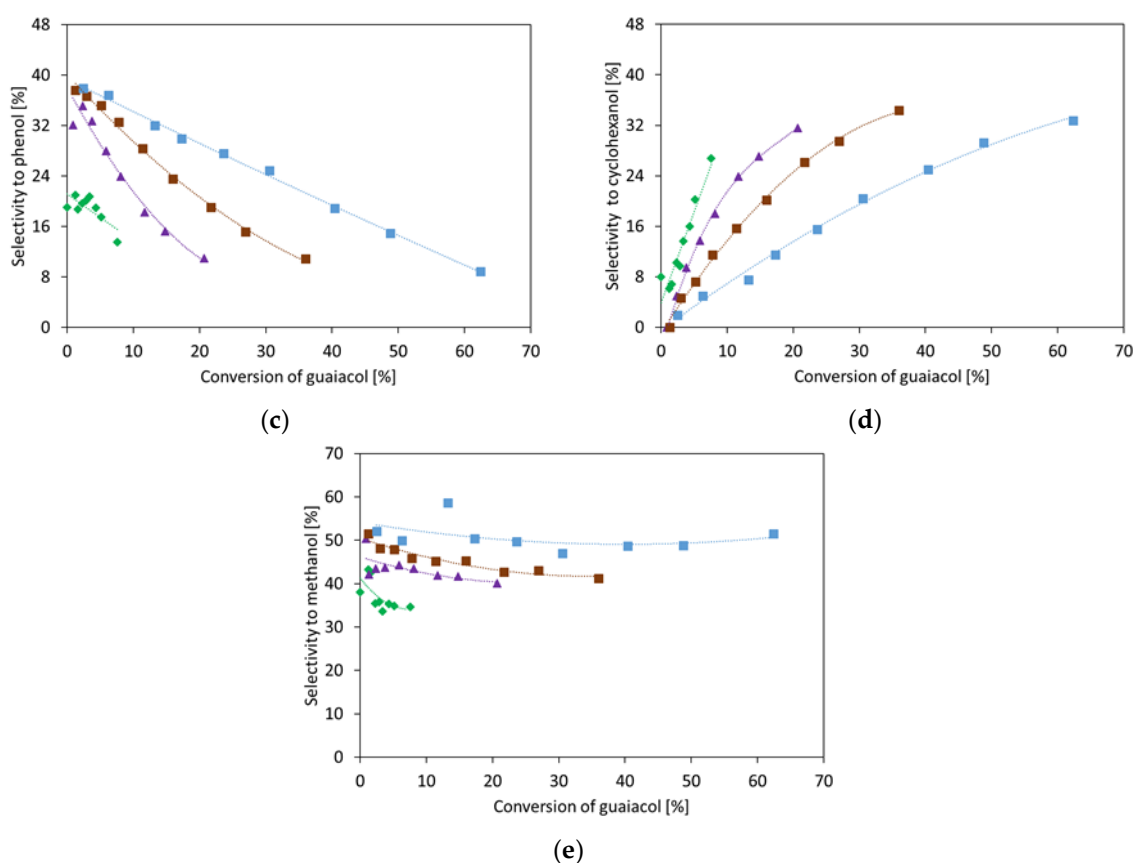


Figure 5. (a) Conversion of guaiacol. Selectivity to (b) methoxycyclohexanol, (c) phenol, (d) cyclohexanol, and (e) methanol at 70 °C in guaiacol:furfuryl alcohol mixtures of 100:0, 90:10, 80:20, and 50:50 mol:mol.

The presence of furfuryl alcohol and its hydrogenated products in the reaction mixture caused a dramatic change in the product selectivity. With the increase in furfuryl alcohol content in the reaction mixture, the selectivity to the direct hydrogenation pathway of guaiacol increased at the expense of demethoxylation, as seen by the selectivity to methoxycyclohexanol and phenol, respectively (Figure 5b,c, Figure S2). The promoted hydrogenation pathway (or suppressed demethoxylation pathway) was also documented by the increased selectivity to cyclohexanol and the decreased selectivity to methanol (Figure 5d,e, Figure S2).

In contrast, furfuryl alcohol was converted much faster in the mixture with guaiacol than when hydrogenated pure (Figure 6a). This can be attributed to the competitive adsorption between guaiacol and furfuryl alcohol where FFOH is more strongly adsorbed and hence the surface becomes preferentially occupied by FFOH and its products. On the one hand, it led to suppressed guaiacol conversion (as shown above) and, on the other hand, to very fast conversion of FFOH due to—in practice—a very high ratio of catalyst to FFOH. To access the impact of the differences in FFOH-to-catalyst ratios due to the different feed composition, the FFOH conversion was plotted as a function of adjusted time axis (Figure 6b). The data indicate that hydrogenation of furfuryl alcohol was auto-inhibited when the FFOH concentration was 50 mol% or higher. On the other hand, when the FFOH concentration was 10 or 20 mol%, the inhibition effect was not observed (Figure 6b). The changes in the selectivity to FFOH-derived products with the change of guaiacol-to-FFOH ratio were not as pronounced as in the case of guaiacol (Figure 6c–f). Nonetheless, it was clear that selectivity towards the intermediate DHFFOH decreased with the decreasing concentration of guaiacol in the reaction mixture. At the same time, the selectivity towards 1,2-pentanediol and 1,5-pentanediol was enhanced (Figure 6e,f). Due to the high reaction rate and reaching the full conversion of FFOH in the first 50 min,

the selectivities towards reaction products are presented as a function of reaction time rather than conversion used in the case of guaiacol.

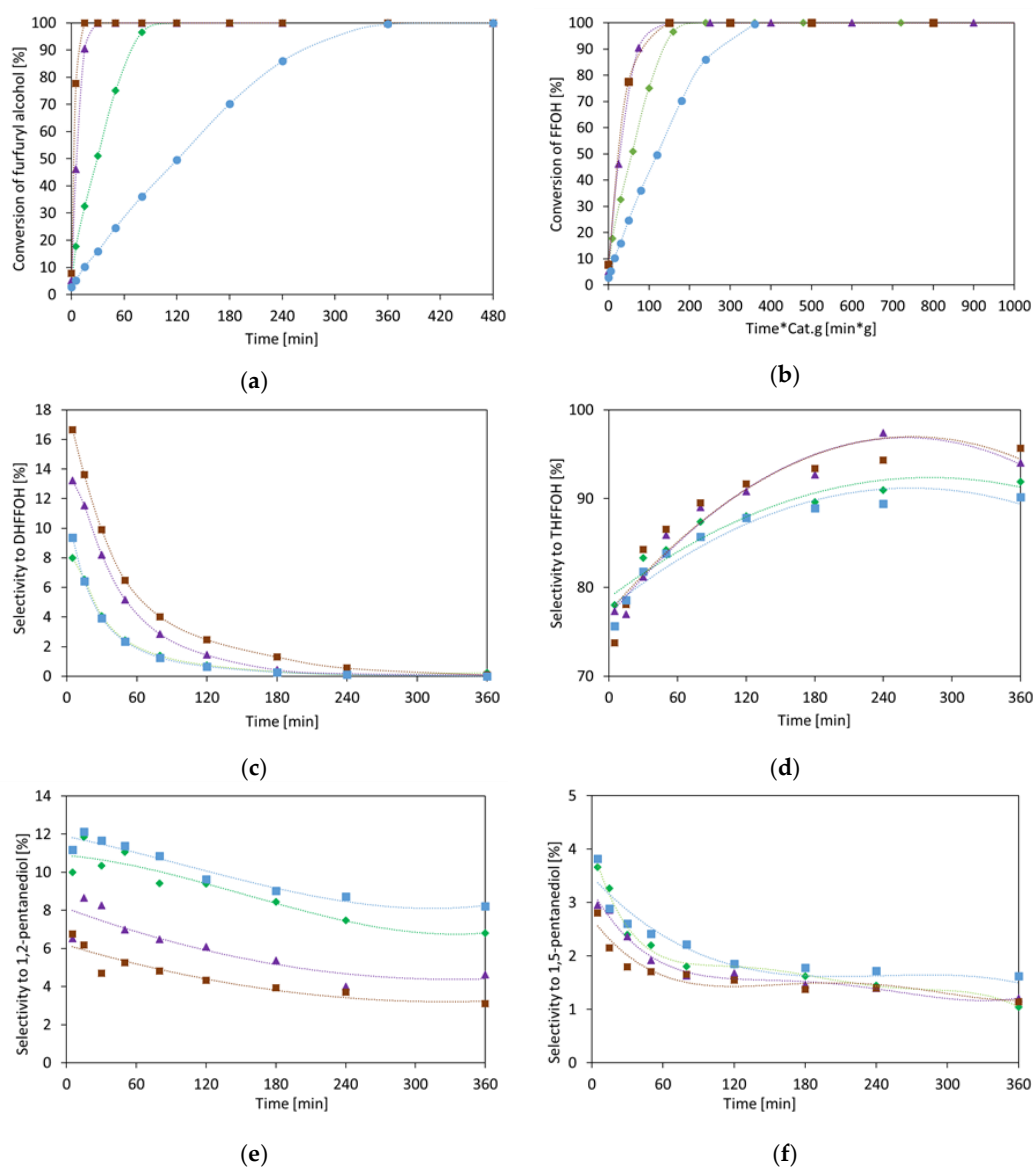


Figure 6. (a) Conversion of FFOH, (b) hydrogen consumption. Selectivity to (c) DHFFOH, (d) THFFOH, (e) 1,2-pentenediol, and (f) 1,5-pentenediol at 70 °C in guaiacol:furfuryl alcohol mixtures of 90:10, 80:20, 50:50, 0:100 mol:mol.

2.2.2. Methyl Isobutyl Ketone with Furfuryl Alcohol

The addition of furfuryl alcohol (10–50 mol%) to methyl isobutyl ketone affected the conversion of MIBK much less than it influenced the guaiacol conversion. This can be attributed to the fact that the conversion of MIBK is more facile than that of guaiacol as described above. Full conversion of MIBK for mixture 90:10 and almost full conversion for the 80:20 mixture was reached at the end of the reaction period. However, in the 50:50 mixture, the conversion of MIBK was only 64% after 360 min. Again, as in the experiment with neat MIBK, 4-methyl-2-pentanol was the only reaction product of MIBK hydrogenation. Interestingly, the conversion curve of MIBK in the 90:10 mixture had the same shape as for neat MIBK hydrogenation, but in the 50:50 mixture it exhibited an S-shaped curve. Because the reaction rate of MIBK hydrogenation increased at about the same time when FFOH was fully converted (at about 120 min, Figure 7a,b), it can be concluded that the strong adsorption of FFOH

and, consequently, the high surface coverage of FFOH prevented MIBK hydrogenation. Once FFOH was hydrogenated, hydrogenation of MIBK occurred rather easily. The hydrogenation of MIBK in the 80:20 mixture confirms this conclusion, as there was also an indication of the S-shaped curve with the inflex point at about 20–30 min (Figure 7a) that again corresponded to the full conversion of FFOH (Figure 7b).

Due to the preferential adsorption of FFOH (in comparison with MIBK), its conversion increased with the decreasing concentration of FFOH in the reaction mixture (Figure 7b). Nonetheless, the reaction pathway of FFOH conversion into THFFOH was unaffected. The product composition (i.e., selectivity to THFFOH and both diols) was constant as soon as FFOH and the DHFFOH intermediate were fully hydrogenated. It can thus be inferred that 1,2-pentanediol and 1,5-pentanediol were not formed by hydrogenolysis of the C–O in THFFOH over Raney-Ni under mild reaction conditions. In other words, both diols were formed by the hydrogenolysis of the C–O bond in a partially hydrogenated intermediate—that is, either DHFFOH or in adsorbed partially saturated surface intermediates.

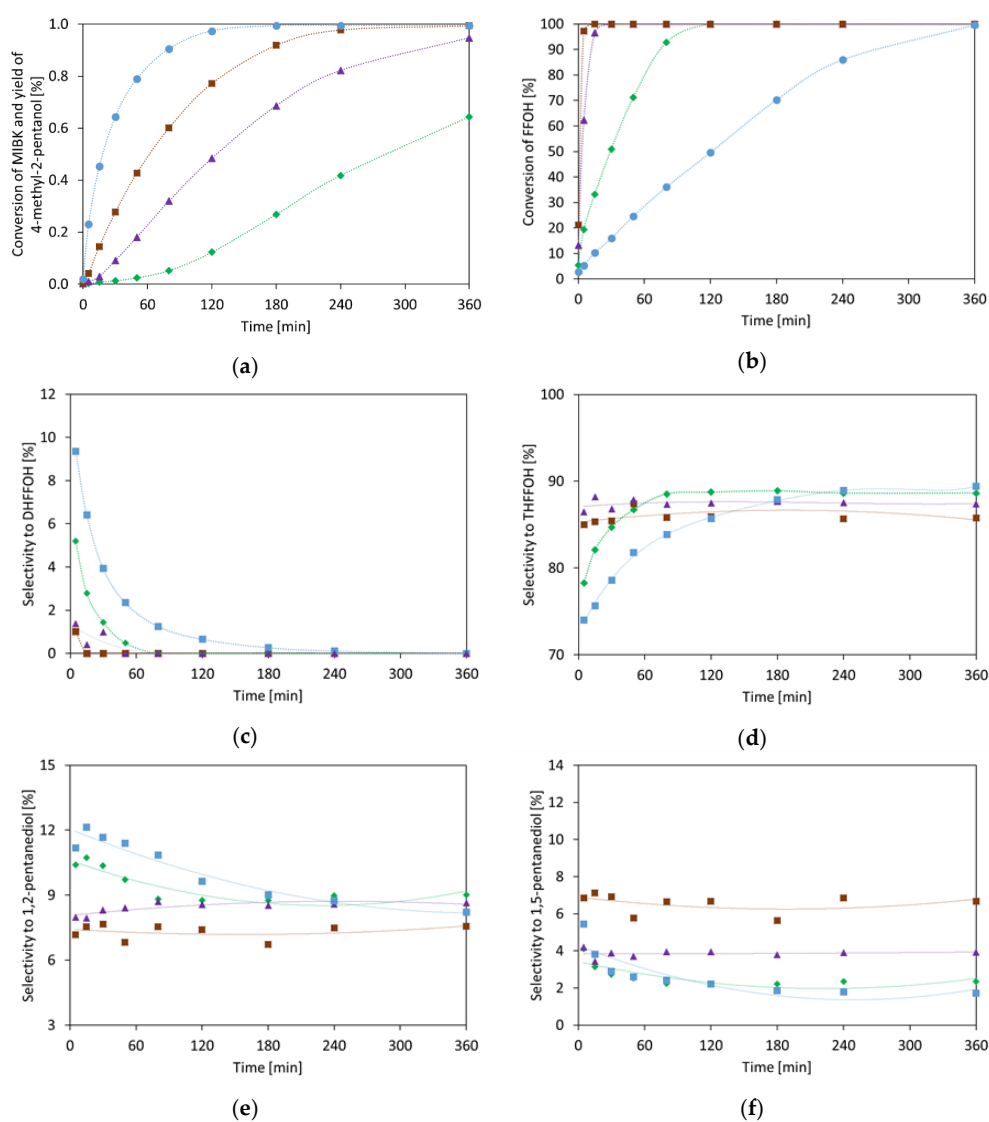


Figure 7. (a) Conversion of methyl isobutyl ketone (MIBK) and yield of 4-methyl-2-pentanol; (b) Conversion of FFOH. Selectivity to (c) DHFFOH, (d) THFFOH, (e) 1,2-pentenediol, and (f) 1,5-pentenediol at 70 °C in MIBK:furfuryl alcohol mixtures of 100:0, 90:10, 80:20, 50:50, and 0:100 mol:mol.

2.2.3. Guaiacol with Methyl Isobutyl Ketone

Having established the pronounced effect of furfuryl alcohol hydrogenation on both guaiacol and methyl isobutyl ketone hydrogenation, we decided to investigate also the mutual inhibition effects in the guaiacol–MIBK mixtures. Hence, the following reaction mixtures of guaiacol to MIBK were studied: 5:95, 20:80, 50:50, and 80:20 mol:mol. Results of their hydrogenation at 70 °C are presented in Figure 8.

The conversion data clearly indicate that the conversion of MIBK was only slightly suppressed by guaiacol, in contrast to the influence of FFOH. At the same time, it is obvious from the very high guaiacol conversions at its low concentration in the mixture with MIBK that guaiacol was hydrogenated preferentially. This can be ascribed to its stronger adsorption in comparison with MIBK. The increasing MIBK concentration in the mixtures resulted in an increased selectivity to cyclohexanol at a given conversion and a decreased selectivity to methoxycyclohexanol. This indicates that in the presence of MIBK, the demethoxylation pathway was preferred to the direct hydrogenation.

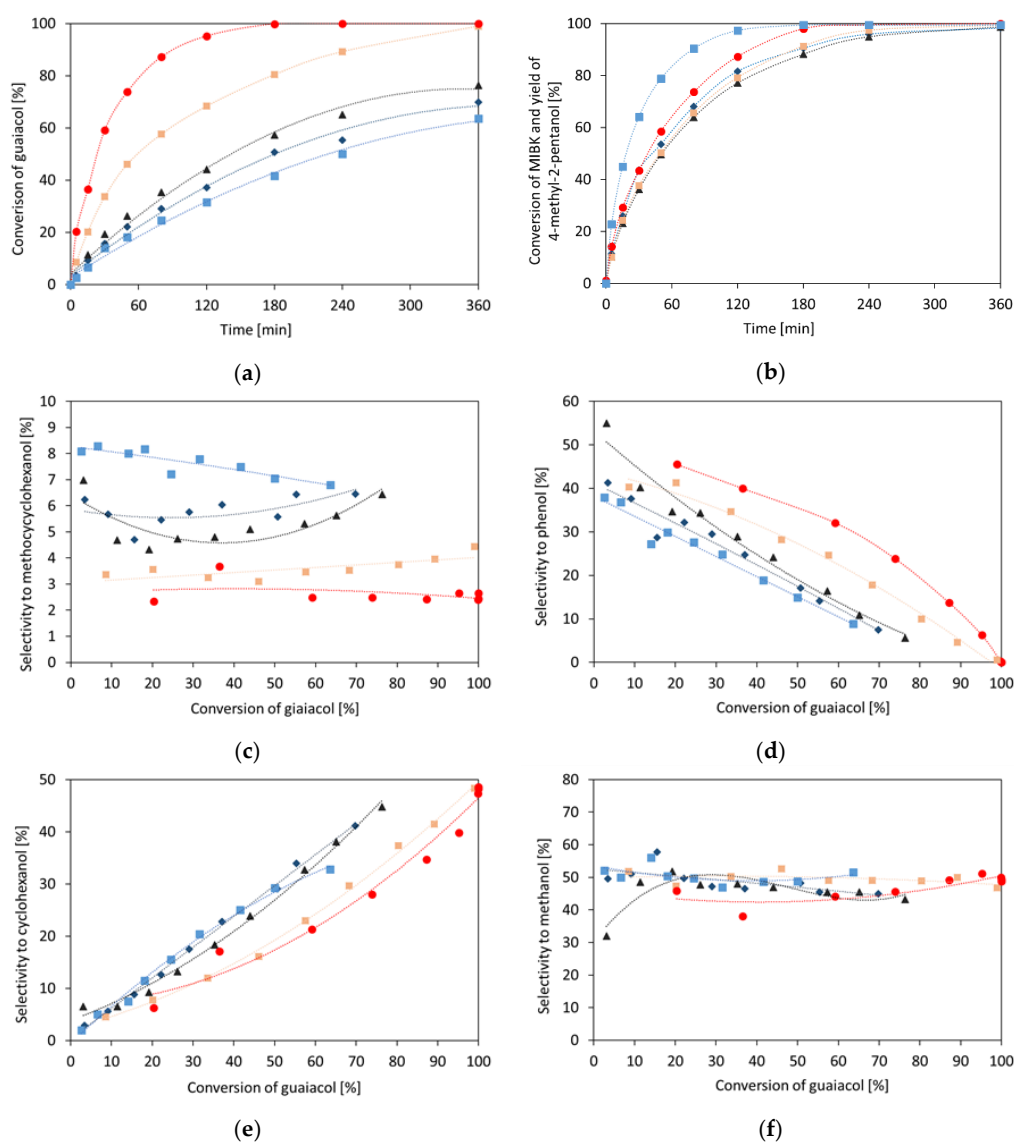


Figure 8. (a) Conversion of guaiacol; (b) Conversion of MIBK and yield of 4-methyl-2-pentanol. Selectivity to (c) methoxycyclohexanol, (d) phenol, (e) cyclohexanol, and (f) methanol at 70 °C in guaiacol:MIBK mixtures of 5:95, 20:80, 50:50, and 80:20 mol:mol as well as pure guaiacol and MIBK, marked with blue squares.

Additionally, we decided to explore the temperature dependency of the conversion for a selected guaiacol:MIBK mixture. We chose a 50:50 mol:mol mixture and carried out its hydrogenation at 50 and 30 °C, to compare it with the already presented results at 70 °C. Results of these experiments are shown in Figure 9. As expected, the decrease in temperature resulted in a lower conversion of both reactants. Nonetheless, the changes in MIBK conversion were negligible (in contrast with the experiment with neat MIBK—see above). This can be explained by the fact that, due to the high activation energy, guaiacol was converted very slowly at low temperatures and did not compete efficiently with MIBK for the active hydrogenation sites. In contrast, at 70 °C the conversion of MIBK was slightly suppressed in comparison with neat MIBK conversion experiments, which was caused by the competitive adsorption and hydrogenation of guaiacol and MIBK at 70 °C. The product distributions indicate (Figure 9c–f) that direct hydrogenation of guaiacol was enhanced at the expense of demethoxylation at low temperatures.

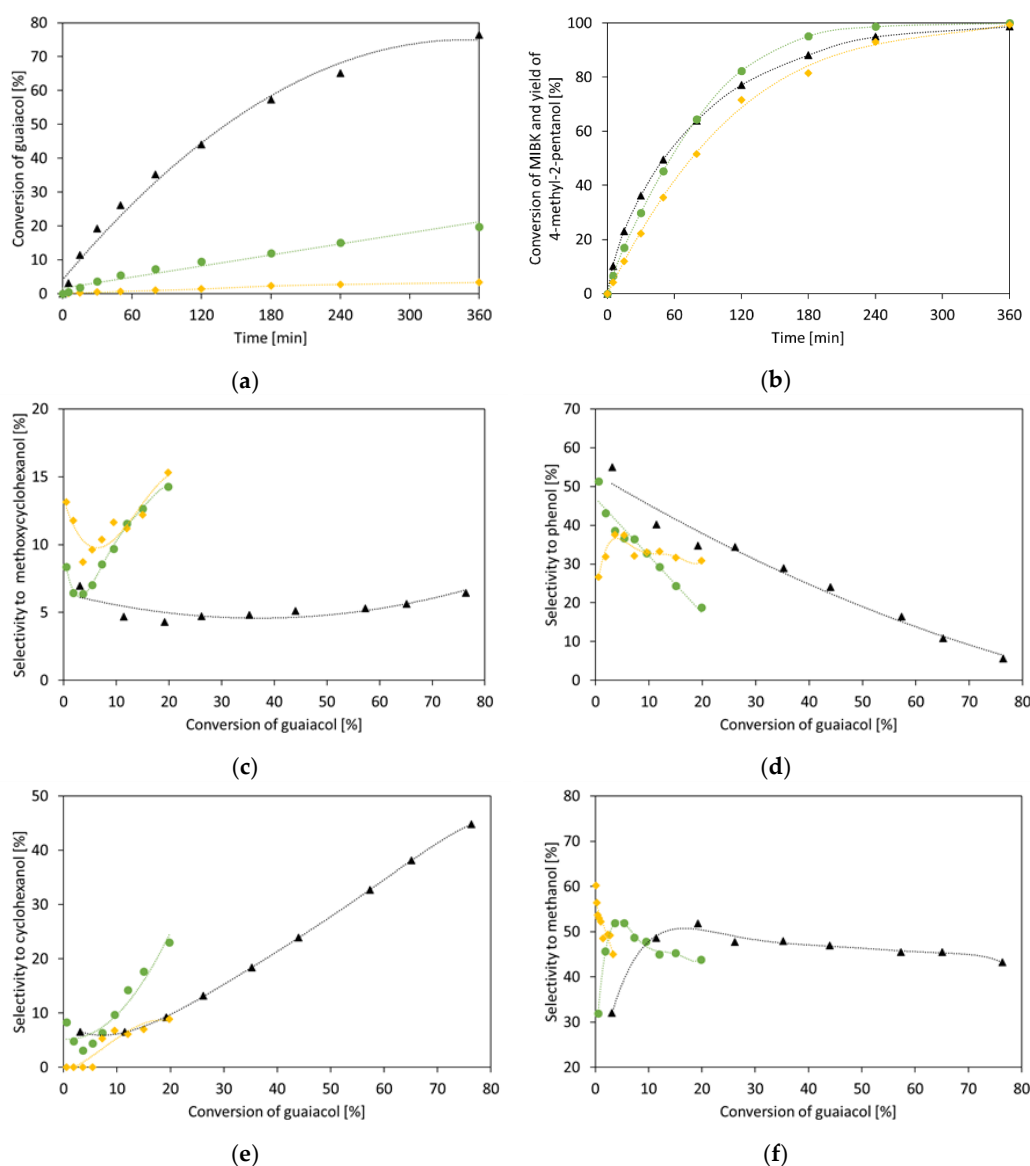


Figure 9. (a) Conversion of guaiacol; (b) Conversion of MIBK and yield of 4-methyl-2-pentanol. Selectivity to (c) methoxycyclohexanol, (d) phenol, (e) cyclohexanol, and (f) methanol at 30, 50, and 70 °C in 50:50 mixtures of guaiacol:MIBK (mol:mol).

3. Materials and Methods

3.1. Chemicals

The following oxygenated model compounds representing different bio-oil compounds were used in the experiments, either pure or in a mixture: guaiacol, furfural, furfuryl alcohol, and methyl isobutyl ketone (all >99%, Sigma-Aldrich, s.r.o., Prague, Czech Republic). Isopropyl alcohol (p.a., Penta, s.r.o., Prague, Czech Republic) was used as a solvent in the experiments. Hydrogen gas (99.9 vol%, SIAD Czech, s.r.o., Prague, Czech Republic) was used as a hydrogen source, and Raney®-Ni (Raney2400 in the slurry, Sigma-Aldrich, s.r.o., Prague, Czech Republic) was used as a catalyst.

3.2. Experimental Setup

The hydrogenation of model compounds was carried out in a modified three-neck round-bottom flask 100 mL glass flask (reactor). An overhead cooler was connected to the middle neck. The left neck was used for sampling and feed injection, while hydrogen was supplied through the right neck.

The catalyst (ca. 5 g) was placed in the reactor and covered by 75 mL of solvent (isopropanol). The reactor was then connected to the hydrogen (99.9 vol%, SIAD Czech, s.r.o., Prague, Czech Republic) gas line and an overhead cooler, and was finally placed in a pre-heated silicon oil bath to pre-heat the catalyst–solvent mixture. The whole setup was flushed with nitrogen (99.9 vol%, SIAD Czech, s.r.o., Prague, Czech Republic) for several seconds before it was connected to the hydrogen flow to remove any oxygen from the system. The stirring was set to 400 rpm for all experiments, and once the desired temperature was reached, the feed was injected in the reactor. Typically, ca. 5 g of feed was added in the reactor to obtain a constant feed/catalyst ratio equal to unity. A different feed/catalyst ratio was used in only a few experiments in order to check the influence of this ratio on the reactant conversion and product selectivity.

The first sample was withdrawn by a syringe from the reaction mixture after 15 s to ensure proper mixing of the feed with the catalyst–solvent mixture. The first sample corresponded to time 0 min in each experiment. The syringe was equipped with a syringe filter (13 mm, 0.45 µm, LABICOM, s.r.o., Olomouc, Czech Republic) to remove catalyst from the sample and thus to stop the reaction. The total reaction time was up to 8 h, and several samples were collected during each experiment to determine the changes in the concentration of reactants and products as a function of time. We performed the hydrogenation of FFOH four times under the same reaction conditions (70 °C) to confirm the reproducibility of the experiments. The standard deviation of these experiments was 3%.

3.3. Qualitative and Quantitative Analysis

GC-MS was used to identify the hydrogenation products. The GC-MS instrument consisted of a gas chromatograph Focus GC equipped by a column ZB-5MSi (W/Guardian, 30 m (+5 m Guardian end) × 0.25 mm × 0.25 µm), an autoinjector AI 3000, and a DSQ mass spectrometer (all Thermo-Fisher Scientific, s.r.o., Prague, Czech Republic). The following temperature program was used: hold at 40 °C (5 min), then 10 °C·min⁻¹ to 300 °C and hold at 300 °C (5 min). The instrument control and data processing were performed using Xcalibur 2.2 software (Thermo-Fisher Scientific, s.r.o., Prague, Czech Republic). All samples (≈100 µL) were dissolved in about 1.7 mL of isopropyl alcohol (p.a., Penta, s.r.o., Prague, Czech Republic) prior to the analysis.

To quantify all identified products as well as raw materials, GC-FID HP 5890 (HPST, s.r.o., Prague, Czech Republic) with HP-5 (15 m × 0.32 mm × 0.25 µm) was used. The following temperature program was used: hold at 35 °C (3 min), then 6 °C·min⁻¹ to 280 °C and hold at 280 °C (2 min).

4. Conclusions

The hydrogenation of bio-oil model compounds and their mixtures over Raney-Ni provided insights into mutual inhibition/promotion effects during the upgrading of binary reaction mixtures. Considering the multicomponent composition of bio-oils, this is the first step towards understanding

the complex transformation of bio-oils into green diesel components and designing efficient catalysts for this transformation.

Raney-Ni catalyst under mild reaction conditions (<70 °C, 1 bar H₂) was efficient in the hydrogenation of all unsaturated model compounds. Carbonyl groups (in furfural and in methyl isobutyl ketone) were easily hydrogenated to the corresponding alcohols, and the aromatic rings (i.e., benzene ring in guaiacol and furanic ring in furfuryl alcohol) were saturated to the corresponding naphthenic rings. Demethoxylation of guaiacol was the only deoxygenation reaction that took place under the mild reaction conditions. It can be thus inferred that already at very mild conditions the most reactive model compounds could be stabilized, but not deoxygenated (except demethoxylation).

The experiments with binary mixtures of model compounds showed a strong influence of furfuryl alcohol on the hydrogenation of the other model compounds. The strong preferential adsorption of furfuryl alcohol on the active sites caused a dramatic decrease in the conversion of guaiacol and methyl isobutyl ketone. In the case of guaiacol, the selectivity to hydrogenation and demethoxylation reaction pathway was affected by the presence of furfuryl alcohol in the reaction mixture. The increasing concentration of furfuryl alcohol in the binary mixture with guaiacol resulted in a decreasing selectivity to the demethoxylation products. Moreover, guaiacol negatively affected the conversion of methyl isobutyl ketone, although less than furfuryl alcohol.

These results show that the composition of bio-oils plays a key role in the efficiency of hydrogenation catalysts used for their upgrading. It also follows that the use of neat model compounds is not appropriate to characterize the efficiency of hydrogenation catalysts in bio-oil upgrading to green diesel components, and more complex model mixtures have to be used.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/3/268/s1>, Figure S1. Conversion of guaiacol at 1:2, 1:1 and 2:1 feed-to-catalyst ratio., Figure S2. Selectivity to (a) methoxycyclohexanol, (b) phenol, (c) cyclohexanol, and (d) methanol at 30, 50, and 70 °C for pure guaiacol.

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