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Heterogeneously catalyzed reactive extraction for biomass valorization into chemicals and fuels

Abstract: This paper focuses on the heterogeneously catalyzed reactive extraction and separation in reaction steps in organic and aqueous phases during the transformation of biomass derived products. Two approaches are demonstrated for decomposing and preserving routes for biomass transformation into valuable products. The decomposing approach has been validated by transformation of glycerol into building blocks like CO, CO_2 and H_2 by aqueous phase reforming (APR) in the aqueous phase with simultaneous synthesis of hydrocarbons by Fischer-Tropsch synthesis (FTS) in the organic phase. The preserving approach has been validated by the dehydration of xylose over acidic catalyst with the hydrogenation of formed furfural in the organic phase. As a result, selectivities in the range of 30–50% to the wax and tetrahydrofurfuryl alcohol, respectively, have been obtained by application of reactive extraction for both approaches.

Keywords: aqueous phase reforming; biomass; dehydration; Fischer-Tropsch synthesis; reactive extraction.

1 Introduction

Biomass is supposed to become one of the main resources for the synthesis of chemicals and fuels in the near future to substitute limited fossil fuels. There are

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two general chemical ways of biomass transformation into valuable products: decomposition (decomposing route) to simplest building blocks like bio-syngas during gasification (BTL technology) with subsequent synthesis of hydrocarbons during Fischer-Tropsch synthesis (FTS) [1], and mild transformation saving C-C (preserving route) bonds like during dehydration or oxidation of saccharides [2]. Both of these ways have their own advantages and drawbacks.

Biomass gasification implies decomposition of solid or liquid carbonaceous material at higher temperatures (700–1000°C) during reaction with air, oxygen, and/or steam into syngas containing CO, H_2, CO_2, CH_4 and N_2 in various proportions [3]. The syngas produced from biomass usually has relatively low H_2/CO ratios (0.5–1) in comparison with methane steam reforming; it contains significant amounts of CO_2, several ppm of sulfur and a few other impurities which can contaminate the catalysts for bio-syngas valorization [4]. In addition, gasification requires preliminary drying of biomass. In a second step of BTL technology, a cleaning process is applied to the bio-syngas in order to remove impurities, resulting in clean bio-syngas which meets the FTS requirements [5]. The produced syngas might be used for the synthesis of different products (Figure 1). Synthesis of methanol over Cu-based catalysts with subsequent dehydration over acidic catalysts leads to the formation of dimethyl ether (DME) [6] which is considered as a clean alternative diesel fuel because of a high cetane number, low auto-ignition temperature and reduced emission of contaminants [7]. FTS is considered the main tool for transformation of bio-syngas into hydrocarbons like olefins and diesel range hydrocarbons [8–10]. Due to the low H_2/CO ratio, direct utilization of this H_2-poor syngas inside a FTS reactor is possible only if the water-gas-shift (WGS) reaction occurs simultaneously, providing a high enough molar H_2/CO ratio throughout the reactor. It significantly restricts use of active Co, Ru-based catalysts and requires application of less active Fe-based catalysts.

The preserving route includes several possible ways depending on the type of biomass or biomass derived chemicals. One of the most common ways involves hydrolysis of cellulosic biomass with formation of saccharides like glucose, fructose, xylose etc. However,
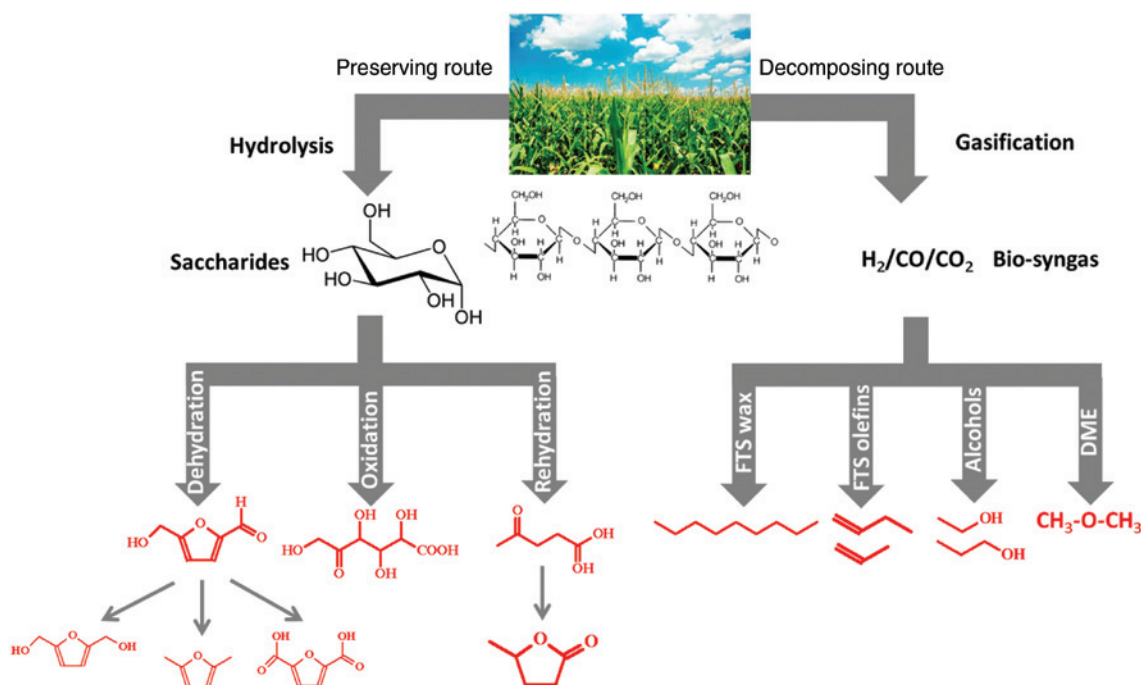
Figure 1: Scheme of biomass valorization.

additional stages are necessary here to prepare and purify the biomass and products, which makes produced saccharides still expensive for industry in comparison with bio-syngas in the decomposing route [11] (Figure 1). These chemicals might be further transformed into valuable products. For example, direct oxidation of glucose is used for the synthesis of gluconic acid, which is an important intermediate in the food and pharmaceutical industries [12]. Dehydration of monosaccharides over acidic catalysts leads to the synthesis of furfural compounds. The product of dehydration should be further treated for the synthesis of chemicals and fuels. Mild hydrogenation of 5-hydroxymethylfurfural (HMF) for example leads to 2,5-bis-(hydroxymethyl)tetrahydrofuran which is used for the synthesis of polyesters [13]. 2,5-Dimethylfuran forms by hydrogenation of formyl and hydroxyl groups of HMF and has high potential as a liquid fuel [14]. Catalytic hydrogenation of levulinic acid as the product of rehydration leads to the formation of γ-valerolactone (GVL), which is one of the most interesting compounds for the industry (fuel, solvent) [15].

Thus, the preserving route leads to the synthesis of high added value products, although it requires special pretreatment stages. In the case of the decomposing route, the range of products is limited; however, all types of biomass might be used for bio-syngas production. Both ways suffer from the number of stages with intermediate separation and purification of the product. The best way

would be transformation of biomass into fuels and chemicals directly in one reactor, which would significantly save energy and resources due to the higher selectivity of the process.

There are several issues that need to be clarified in the case of a combination of different processes in one reactor such as:
– Interaction of the catalysts of different nature leading to deactivation;
– Undesired reactions due to the catalytic conversion of the chemicals and intermediate products over catalysts in the same phase;
– Different conditions for different processes (temperature, pressure).

This work aims at developing novel strategies to enhance the efficiency of combined processes for synthesis of fuels and chemicals from biomass. This strategy is based on a biphasic reactor with localization of the hydrophobic catalyst for hydrogenation processes in the organic phase and localization of the hydrophilic catalyst in the aqueous phase with reactive extraction of intermediate products into the organic phase during transformation of biomass derived products in the aqueous phase. In this case, problems are easily solved due to the absence of direct contact between the hydrophobic and the hydrophilic catalyst. The undesired contact between the hydrophobic catalyst and intermediate or parent biomass

products can be avoided. A combination of FTS and aqueous phase reforming (APR) of glycerol and dehydration of xylose to furfural with further hydrogenation into THFA were chosen as examples of the destructing and preserving valorization routes, respectively (Figure 2). The process in the aqueous phase is the first step of biomass decomposition. In the case of the preserving route, the first step is dehydration of sugars to furfurals at mild conditions, with the temperature similar to the temperature of hydrogenation over metallic catalysts (130–170ºC) (Figure 2). In the case of the destructive route, biomass gasification will be substituted by the recently uncovered APR process [16] (Figure 2). The main advantage of APR compared to gasification is the lower temperature (200–250°C) [16]. In addition, the APR operating conditions are similar to the conditions of low temperature FT synthesis. These reactions, therefore, might be combined in one reactor.

2 Materials and methods

2.1 Catalyst preparation

The powdered ruthenium on a carbon catalyst (Ru-C) containing 5 wt.% Ru was prepared by incipient wetness impregnation of the hydrophobic carbon (CEKA S.A.) by an aqueous solution of $RuCl_3$ (Sigma-Aldrich). The Pt-Al_2O_3 catalyst with 5 wt.% Pt was prepared by incipient wetness impregnation of alumina powder (Puralox SCCA 5/170, Sasol) by an aqueous solution of $(Pt[NH_3]_4)(NO_3)_2$

(Sigma-Aldrich). The catalysts were dried at 100°C and reduced in H_2 atmosphere at 500°C. Afterwards, the catalysts were passivated in a flow of He at ambient temperature. Amberlyst-15 in hydrogen form with 50% water was purchased from Sigma-Aldrich.

2.2 Catalysis

Experiments were carried out in a stirred autoclave working in batch mode and equipped with several valves for sampling the liquid (aqueous and organic) and gas phases. All reagents were purchased from Sigma-Aldrich.

The procedure for testing the catalysts in the preserving route was as follows: xylose (10 g), Ru-C catalyst (0.4 g), Amberlyst-15 catalyst (10 g), water (300 ml) and organic solvent (300 ml, in the case of experiments with solvent) were poured into the autoclave. The autoclave was purged with hydrogen, the temperature was increased to 165°C or 135°C and thereafter, the catalytic experiment was started. The pressure of hydrogen was kept at 2.5 MPa.

The procedure for testing the catalysts in the decomposing route was as follows: water (40 ml), 5 g glycerol and Pt-Al_2O_3 (0.5 g) in the aqueous phase and decane (10 g) with catalyst Ru-C (0.5 g) in the organic phase. The aqueous and organic phases were poured into the autoclave. H_2SO_4 (0.1 m) was added to the aqueous phase in the case of the experiment with acid addition. In the case of experiments for FT synthesis, the autoclave was purged and filled with CO (10 bar) and hydrogen (20 bar). The autoclave was purged and filled with N_2 (5 bar), the temperature was increased to 220°C and thereafter, the catalytic experiment was started.

The stirring rate was 300 rpm. This speed provided adequate mixing in each phase without a transfer of catalysts between the phases.

Periodically, gas and liquid samples were taken from the autoclave. The amount of xylose, xylitol and glycerol in the samples was
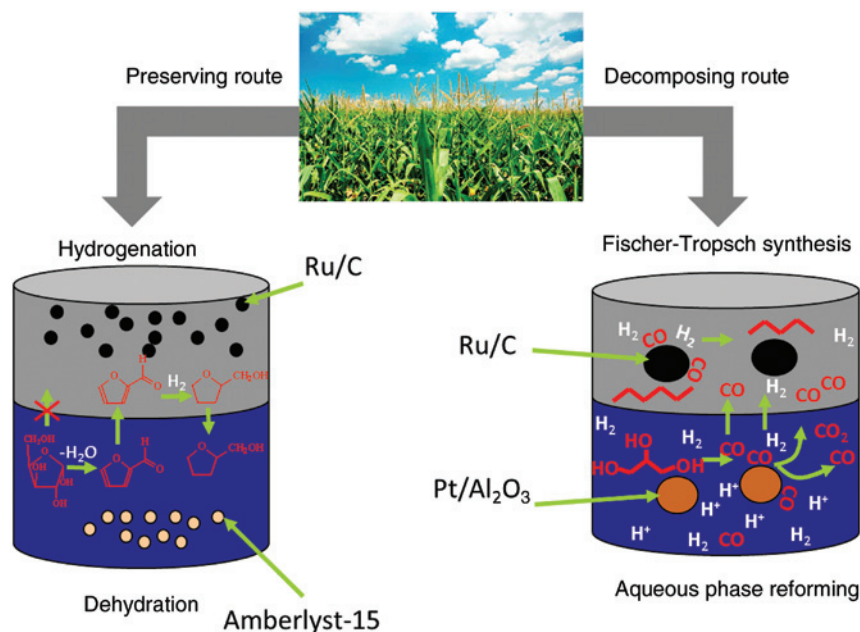

Figure 2: Scheme of reactive extraction for biomass valorization according to decomposing and preserving routes.

analyzed by HPLC (Shimadzu). Furfural, the products of its hydrogenation during dehydration-hydrogenation, and light hydrocarbons formed during combined APR-FTS were analyzed by gas chromatography (Bruker). Simulated distillation by gas chromatography was used to analyze the long chain hydrocarbons (C_{12}-C_{60}).

Conversion of xylose (mol %) and product selectivity (mol %) was defined as follows:

$$\text{Conversion (mol \%)} = \frac{\text{moles of xylose reacted}}{\text{moles of initial xylose}} \times 100.$$

$$\text{Selectivity (mol \%)} = \frac{\text{moles of product produced}}{\text{moles of xylose reacted}} \times 100.$$

Conversions of glycerol (mol %) and product selectivity (mol %) in APR and combined APR-FTS were defined as follows:

$$\text{Conversion (mol \%)} = \frac{\text{moles of reacted glycerol}}{\text{moles of initial glycerol}} \times 100.$$

$$\text{Selectivity to C containing products (mol \%)} = \frac{\text{moles of C atoms of product produced}}{3 \times \text{moles of reacted glycerol}} \times 100.$$

$$\text{Selectivity to H}_2 \text{ (mol \%)} = \frac{\text{moles of H}_2 \text{ produced}}{7 \times \text{moles of reacted glycerol}} \times 100.$$

3 Results

3.1 Transformation of biomass in aqueous phase without reactive extraction

3.1.1 Preserving route

Dehydration of xylose results in furfural as the main product of the reaction. In the aqueous phase, a sharp decrease in the selectivity to furfural from 80% to 20% was observed with an increase in the xylose conversion up to 70% (Figures 3 and 4). Xylose dehydration in the
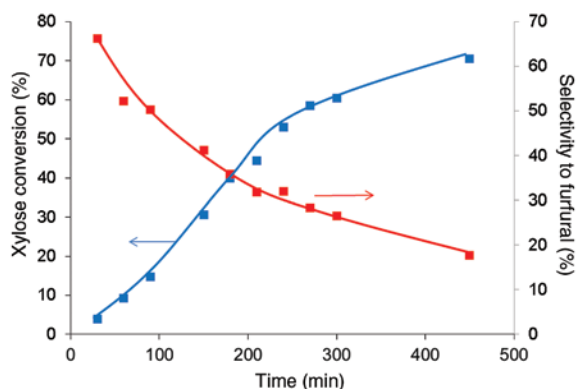
Figure 4: Distribution of the products during xylose dehydration and the combined process of xylose dehydration-hydrogenation (165°C , xylose 10 g, water 300 ml, solvent 300 ml, Amberlyst-15 10 g, Ru-C 0.4 g) at the conversion of xylose of about 70% (except test at 135°C with conversion 32%).

aqueous phase in the absence of organic solvent leads to intensive secondary condensation of the formed furfural with formation of soluble and insoluble humins [17]. The same processes have been observed during dehydration of fructose and glucose over acidic catalysts [18, 19]. A biphasic system with an organic solvent is used for saccharides dehydration in order to preserve furans by its extraction from further condensation [18, 19]. However, in this case furfural is still distributed between the aqueous and organic phases (Table 1). This means that the process of secondary transformation of furfural cannot be totally suppressed. This is why reactive extraction of furfural might not only be used directly for the synthesis of the final product, but also for suppression of furfural transformation into humins.

3.1.2 Decomposing route

APR of glycerol over a metal-based catalyst according to the reaction scheme should lead mainly to the synthesis of H_2 and CO_2: $C_3O_3H_8 + 3H_2O = 3CO_2 + 7H_2$ [16]. Carbon monoxide is assumed to be an intermediate product during

Figure 3: Time dependence of xylose conversion and furfural selectivity during xylose dehydration in aqueous phase (165°C, xylose 10 g, water 300 ml, Amberlyst-15 10 g).
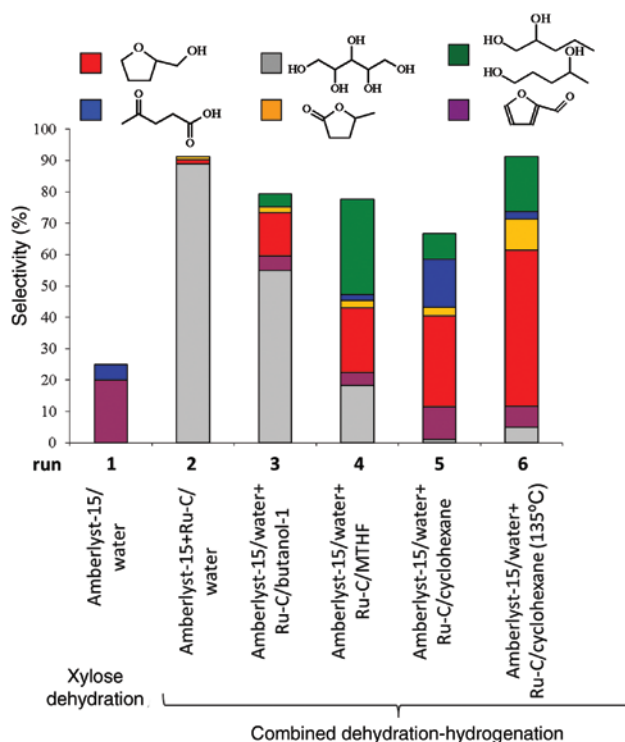
Table 1: Dielectric constants, solubility of biomass derived products, and partition ratio of intermediate products for both preserving and decomposing routes.

Solvent	Dielectric constant	Solubility of xylose/glycerol, $\mu mol/g$	Partition ratio $R=C_{org}/C_{aq}$ for intermediate product
Preserving route			
1-Butanol	17	15.7	Furfural – 3.9
MTHF	7	3.6	Furfural – 7.0
Cyclohexane	2	0	Furfural – 0.7
Decomposing route			
Decane	1.8	0	H_2-6, CO-12

MTHF, methyltetrahydrofuran.

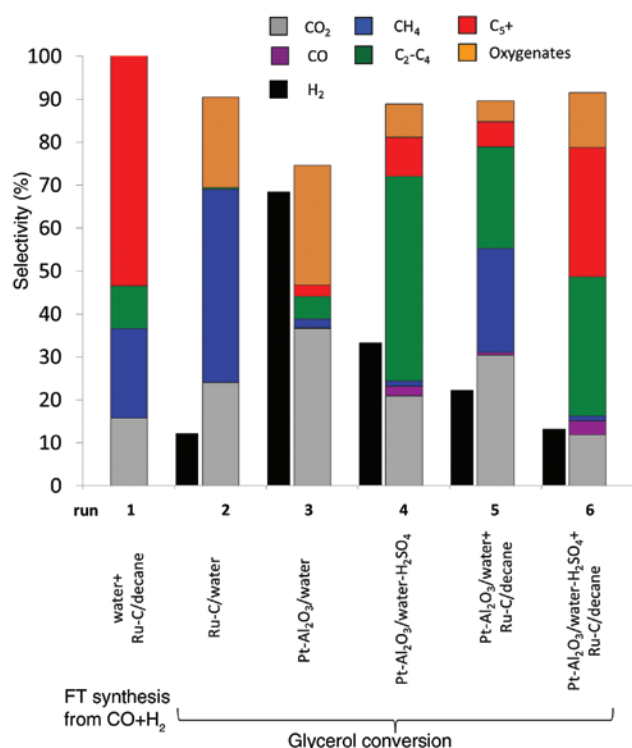**Figure 5:** Distribution of the products during FT synthesis (T=220°C, 40 ml of water, 10 ml of decane, 0.5 g Ru-C, p[CO]=10 bar, p[H_2]=20 bar , conversion of CO 80%), APR and the combined process APR-FTS (T=220°C, 40 ml of water with 5 g glycerol, 0.1 M H_2SO_4, 0.5 g Pt-Al$_2$O$_3$, 10 g decane, 0.5 g Ru-C, p[N_2]=5 bar) at the conversion of glycerol of about 60%.

APR, however, the conditions of the reaction are favorable for the subsequent WGS reaction [20]. Figure 5 shows the distribution of the products during APR of glycerol over Pt-Al$_2$O$_3$ (run 3). Indeed, the main products of the reaction are H_2 and CO_2 with selectivities of 68% and 32%, respectively. Only trace amounts of CO were detected. The process also results in significant formation of the

intermediate oxygenated products like methanol, ethylene glycol, and so on (Figure 5), which could be further converted to H_2 at higher conversion.

A higher concentration of carbon monoxide in the APR products is required, however, for efficient liquid hydrocarbon synthesis using the FT reaction. Our experiments indicated that addition of H_2SO_4 to the aqueous phase significantly affected the selectivity of the WGS reaction over Pt-Al$_2$O$_3$ [21]. The presence of acid in the aqueous phase seems to affect the equilibrium of the WGS reaction by binding with water molecules. Addition of sulfuric acid up to 0.1 M concentration leads to a decrease in the CO_2 selectivity from 36% to 20% and H_2 selectivity from 68% to 33% (run 4, Figure 5). The selectivity to CO, however, remained relatively low (2.3%). At the same time, the selectivity to light hydrocarbons (ethane and propane) increased to 47%. It was shown earlier that addition of acid catalysts (e.g. zeolite) during APR of sorbitol and xylitol over Pt catalysts led to a higher yield of lighter hydrocarbons [22, 23]. Thus, besides a partial shift of the equilibrium in the direction of CO formation during APR, side processes of alcohols dehydration with subsequent hydrogenation takes place in the presence of acid. However, continuous formation of even small amounts of CO might be already enough for its extraction by an organic solvent, due to the high partition coefficients (Table 1) and transformation into hydrocarbons by FT synthesis.

To summarize, the processes of decomposition and preserving character proceed in the aqueous phase with formation of the desired products (furfural, CO, H_2) with subsequent fast transformation into side products. Reactive extraction might be useful here for fast direct transformation of these intermediates into valuable stable products.

3.2 Heterogeneously catalyzed reactive extraction

3.2.1 Preserving route

The main detected products of the combined process of xylose dehydration and furfural hydrogenation in the reaction system were xylitol, furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), levulinic acid, GVL and pentanediols (Figure 4) [24]. Xylitol is the product of xylose hydrogenation over the Ru-C catalyst. FA is the initial product of furfural hydrogenation. Deeper hydrogenation of FA leads to the formation of THFA. Pentanediols should be formed by ring opening of FA during hydrogenation over Ru-C. Rehydration of furfural into levulinic acid takes place over strong acid sites of Amberlyst-15. Subsequent

cyclization during hydrogenation over Ru-C (Figure 4) leads to the formation of GVL.

Addition of the Ru-C hydrogenation catalyst during xylose dehydration in the aqueous phase leads to fast full conversion of xylose with mainly formation of xylitol (90%) as the product of the reaction (run 2, Figure 4). This indicates a faster xylose hydrogenation in comparison with the dehydration. The hydrogenation of xylose to xylitol over Ru catalysts at similar conditions was shown earlier in literature [25].

Thus, combination of xylose dehydration and hydrogenation of formed furfural is impossible in the same aqueous phase. Addition of an organic solvent with localization of the hydrogenation catalyst is necessary. Figure 6 shows the distribution of the hydrophobic Ru-C catalyst between organic (cyclohexane) and aqueous phases before and after reaction. The catalyst is always distributed only in the organic phase, which means that this concept might be used for reactive extraction.

Three different organic solvents with different polarity, solubility of xylose and partition coefficients (Table 1) were used for reactive extraction: 1-butanol, methyltetrahydrofuran (MTHF) and cyclohexane. In the presence of 1-butanol as a solvent, the selectivity of xylose transformation into xylitol is 55% at the similar conversion (run 3, Figure 4). By contrast, in the presence of MTHF and cyclohexane, the selectivity to xylitol is only 20.4% (run 4) and 1.2% (run 5), respectively. This can be explained by a suppression of xylose hydrogenation to xylitol due to the fact that the hydrophobic Ru-C catalyst resides in the organic solvent and that the xylose solubility decreases from 1-butanol to cyclohexane (Table 1). This implies that hydrogenation of xylose, even at the interfacial area, should be accompanied by a partial

solubility of the compound in the solvent. A non-polar solvent like cyclohexane suppresses the hydrogenation of xylose, which is non soluble in this solvent. However, furfural might still be extracted by cyclohexane from water (Table 1).

Simultaneous dehydration and hydrogenation in a single reactor using a butanol-water system leads (in addition to xylitol) to the formation of only 13.9% of THFA and 4.6% of furfural (run 3, Figure 4). The main products in the MTHF-water biphasic system are furfural (17.9%), THFA (23.1%), pentanediols (33.0%) and GVL (1.0%) (run 4, Figure 4). In comparison with the xylose dehydration and hydrogenation in the butanol-water system, the amounts of THFA, pentanediols and GVL are higher in MTHF due to the partial suppression of xylose hydrogenation into xylitol.

The presence of cyclohexane as organic solvent leads to the highest amount of THFA (29%) (run 5, Figure 4). At the same time, high amounts of pentanediols (8.2%), levulinic acid (15.3%), GVL (2.8%) and unreacted furfural (10.4%) were observed. The high amount of unreacted furfural in the presence of cyclohexane indicates a lower rate of furfural hydrogenation over the Ru-C catalyst in comparison with solvents with higher partition ratios (Table 1). The main difference of xylose dehydration combined with hydrogenation over cyclohexane-water in comparison with other biphasic systems is the formation of a high amount of levulinic acid (15.3%). This is the result of the FA presence in the water phase in comparison with other organic solvents.

A decrease of the temperature of the reaction from 165°C to 135°C leads to a significant increase of the contribution of THFA (49.9%), GVL (9.8%) and pentanediols (17.4%) in comparison with the process at 165°C at the similar conversion (run 6, Figure 4). The sum of the hydrogenated products in this case is 92% in comparison to 68% at 165°C. This might be explained by a decrease of side reactions for furfural condensation over Amberlyst-15 and hydrogenation over Ru-C as the temperature decreases.

The alternative process involves dehydration of xylose to furfural, separation of organic phase and hydrogenation of furfural to THFA. For example, dehydration of xylose to furfural over Amberlyst-70 in the water-toluene biphasic system at the similar reaction has been reported to give selectivity to furfural in the range 60–70% [26]. The hydrogenation of furfural to THFA might be processed with high selectivity (90%) over Ni-Pd catalysts in organic solvents [27]. Thus, in the case of a two-stage process, the total selectivity to THFA from xylose might be about 60% which is comparable to the selectivities in the proposed one stage process.
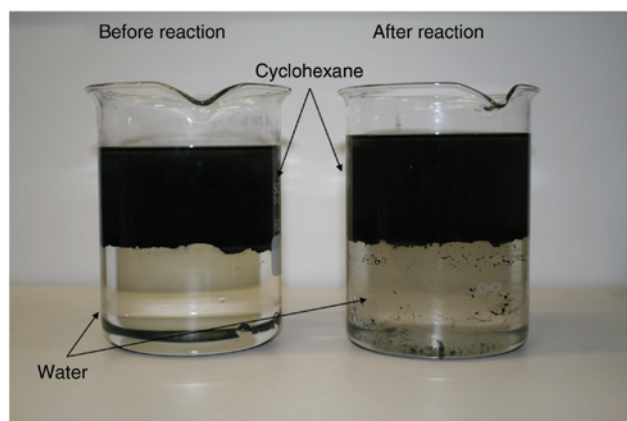

Figure 6: Distribution of the Ru-C catalyst between the aqueous and organic phases before and after dehydration-hydrogenation test.

3.2.2 Decomposing route

The presence of Ru-C in the organic phase in the decomposing route is also very important for several reasons. In the case of Ru-C localization in the aqueous phase, the FT synthesis leads to mostly light alkanes and oxygenates as has been shown earlier [21, 28, 29]. Such a narrow hydrocarbon distribution might be explained by a higher probability of the FT chain termination in the presence of water. To enhance selectivity to heavier hydrocarbons, the Ru catalyst was placed in the organic phase (decane) which was located on the top of the aqueous phase in the biphasic reactor (run 1, Figure 5). The formation of CO_2 by the WGS reaction was significantly suppressed, which was probably due to the lower concentration of water in the organic phase. At the same time, the selectivity to C_5+ long chain hydrocarbons was very high (75.5%) and comparable with selectivities of FT synthesis in organic phases. Thus, because of phase separation in the biphasic reactor, the influence of water on the FT reaction rate and hydrocarbon selectivities seems to be not very significant for the Ru-C catalyst located in the organic phase. The other reason of Ru-C localization in the organic phase can be due to intensive hydrogenolysis of glycerol with formation of methane (run 2, Figure 5). In comparison with the Pt-based catalyst, APR over Ru leads to significantly higher hydrogenolysis activity with intensive formation of methane [30].

The catalytic data obtained for the reactive extraction of syngas during APR are shown in Figure 5 (runs 5 and 6). The process without acid addition to the aqueous phase leads mainly to the formation of methane and light alkanes (run 5, Figure 5). The presence of Ru-C in the organic phase led to a significant decrease in the oxygenate fraction in the products. This might be due to hydrogenation and hydrogenolysis of oxygenates into methane in the presence of hydrogen over Ru-C. A small amount of long chain hydrocarbons (6% of C_5+) was also detected.

Addition of sulfuric acid to the aqueous phase resulted in major changes in the selectivity patterns (run 6, Figure 5). Methane formation was significantly suppressed, whereas the hydrocarbon selectivity shifted to long chain hydrocarbons. Higher selectivity to long chain hydrocarbons in FT synthesis can be attributed to a higher fraction of carbon monoxide produced during APR of glycerol in the presence of acid (run 6, Figure 5). Indeed, the CO_2 selectivity decreases from 30% to 12%, which might be due to the shift of the equilibrium to CO formation with fast extraction of CO into the organic phase. The selectivity to C_5+ hydrocarbons calculated on the basis of carbon atoms of converted glycerol was around 30%.

The increase in the selectivity to hydrocarbons is accompanied by a decrease in the selectivity to oxygenates and light hydrocarbons (methane, ethane). This is the result of the continuous consumption of hydrogen for FTS, which leads to a lower rate of hydrogenolysis.

Catalytic conversion of glycerol by APR and FT synthesis was coupled earlier in a two-bed reactor system consisting of a Pt-Re/C catalyst bed for APR followed by a Ru/TiO$_2$ catalyst bed for FTS [31]. In this case, the shift of the equilibrium in the direction of syngas formation has been attained by lower pressure (5–11 bar) and less WGS active Pt-Re catalyst. Although the process results in the high selectivity to alkanes (30–50%), the products contain a high fraction of gaseous hydrocarbons due to non-optimal conditions for FTS (aqueous phase and low pressure).

Thus, heterogeneously catalyzed reactive extraction has been successfully proven for two ways of biomass valorization according to the preserving and decomposing routes. Selectivities as high as 50% and 30% have been attained for transformation of xylose to THFA and glycerol into C_5+ hydrocarbons. In order to further increase the selectivity, both the catalysts and reaction parameters should be optimized. A close contact between the aqueous phase and the organic phase could be beneficial for fast consumption of produced intermediate products (furfural, CO and H$_2$) in the organic phase before their participation in side reactions in the aqueous phase. This might be achieved by application of an emulsion type system with surfactants for closer contact between the aqueous and organic phases. This concept was successfully used for FT synthesis over Ru-C localized in droplets of the organic phase in the emulsion [32]. The other possible way to increase the contact between the phases in a continuous process is to support the catalysts over packing with a high surface area, like solid foams. Demonstration of this strategy has been performed by a combination of processes via a multilevel rotating foam reactor [33].

4 Conclusion

The concept of heterogeneously catalyzed reactive extraction in the presence of two catalysts in different phases has been successfully proven for the preserving and decomposing routes. The combination of dehydration of xylose over Amberlyst-15 and hydrogenation of extracted furfural over Ru-C has been performed as the preserving route. The main side reaction of the process was hydrogenation of xylose to xylitol, which was suppressed by application of a hydrophobic solvent. The main product of the combined

process was THFA as a result of furfural hydrogenation in the organic phase with a maximal selectivity of 50%.

The combination of APR of glycerol over Pt-Al$_2$O$_3$ with FT synthesis over Ru-C in the organic phase from formed syngas (CO and H$_2$) has been performed as the decomposing route. Addition of sulfuric acid to the aqueous phase led to a higher yield of carbon monoxide in the APR process with significant increase in the selectivity to C$_5$+ hydrocarbons (up to 30%) in the combined process.

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