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Mass transfer effects in the H_2SO_4 catalyzed pivalic acid synthesis

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Abstract

The synthesis of carboxylic acids from alkenes, carbon monoxide and water according to the Koch process is usually carried out in a stirred gas–liquid–liquid multiphase reactor. Due to the complex reaction system with fast, equilibrium reactions and fast, irreversible reactions the yield and product distribution depend on a number of process parameters. The effect of some of these parameters was studied for the production of pivalic acid, using sulfuric acid as a catalyst. For the 96 wt.% sulfuric acid catalyst solution used the main reactions are relatively fast with respect to mass transfer and mixing. Therefore, aspects like the position of the injection point, inlet concentration, agitation intensity and injection rate all influence the yield obtained. The presence of an inert organic liquid phase was found to be beneficial, due to a combined effect of enhanced gas–liquid mass transfer and a 'local supply' effect for carbon monoxide near the hydrocarbon reactant inlet. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: H_2SO_4; Pivalic acid; Alkenes; Mass transfer; Mixing; Multiphase; Gas–liquid–liquid

1. Introduction

The production of sterically hindered carboxylic acids through the Koch synthesis is an example of a complex reaction system with challenging chemical reaction engineering aspects. The production of these Koch acids is generally characterized by the presence of two liquid phases and one gas phase, a parallel/consecutive reaction scheme with fast, equilibrium reactions and fast (irreversible) undesired side reactions. The acid yield and the product distribution obtained for this process depend on a number of process parameters, e.g. temperature, carbon monoxide partial pressure, agitation intensity (liquid mixing), and composition of the catalyst solution. In addition to the desired reaction steps also oligomerization, isomerization and disproportionation reactions may occur. In the present contribution, the effect of some of the process parameters on the acid yield and product composition was studied for the production of the smallest Koch acid, pivalic acid, using sulfuric acid as catalyst solution.

In the industrially applied fully backmixed stirred tank reactors the hydrocarbon reactants and the acids produced constitute a dispersed organic liquid phase. Previous work has shown that the presence of the reaction product in the catalyst phase significantly affects the reaction kinetics [1]. The relatively small reactants used in this study, isobutene and *tert*-butanol, form a gas–liquid two-phase system with the sulfuric acid catalyst phase under the conditions studied. By using heptane as an immiscible liquid phase the effects of this immiscible liquid phase on mass transfer and product yield can be separated from the effects of

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the presence of the reaction products on the reaction kinetics.

2. Reaction mechanism and reaction kinetics

The generally accepted mechanism for the Koch reaction includes four reversible main reaction steps: (I) formation of a carbocation from an alkene or alcohol, (II) addition of carbon monoxide (CO), (III) addition of water and finally (IV) deprotonation of the carboxylic acid formed [2]. The reaction kinetics under Koch reaction conditions (>75 wt.% H_2SO_4) are not well known. Recent work [1] for the kinetics of the pivalic acid formation starting with isobutanol (and in a few experiments *tert*-butanol) as reactant has shown for these reactants that in absence of mass transfer limitations the carbocation formation is rate determining.

In this work the more reactive isobutene and *tert*-butanol have been applied as reactant at high acid concentrations. The rate of protonation under these conditions can be estimated using (extrapolations of) the following correlations:

- isobutene (293 K), [3]
  $\log_{10}(k_{1,\mathrm{app}}) = -1.35\mathrm{Ho} - 3.3 \quad (2 > \mathrm{Ho} > -9)$
- text-butanol (293 K) [1]
  $\log_{10}(k_{1,\mathrm{app}}) = 1.45\mathrm{Ho} - 14.0 \quad (-6.5 > \mathrm{Ho} > -8.5)$

In these correlations $k_{1,\mathrm{app}}$ is the apparent first order (in the alkene concentration) reaction rate constant and Ho is the Hammett acidity function. Details of hydrocarbon solubility in strong sulfuric acid solutions and the correlation used for Ho vs. H_2SO_4 concentration can be found elsewhere [4]. The protonation/dehydration kinetics for *tert*-butanol, as presented above, are determined by measuring the CO consumption rate. When comparing these $k_{1,\mathrm{app}}$ values with dehydration rates for other components, it is found that the apparent protonation rate for *tert*-butanol is much lower than may be expected from dehydration kinetics found in literature for *tert*-pentylalcohol and 2-phenyl-2-propanol [1]. Considering the log–linear relationship with the catalyst solution acidity and the reported carbonylation rates in other media [5], it is most likely that the equilibrium position for the dehydration reaction causes the apparently relatively low CO consumption rate.

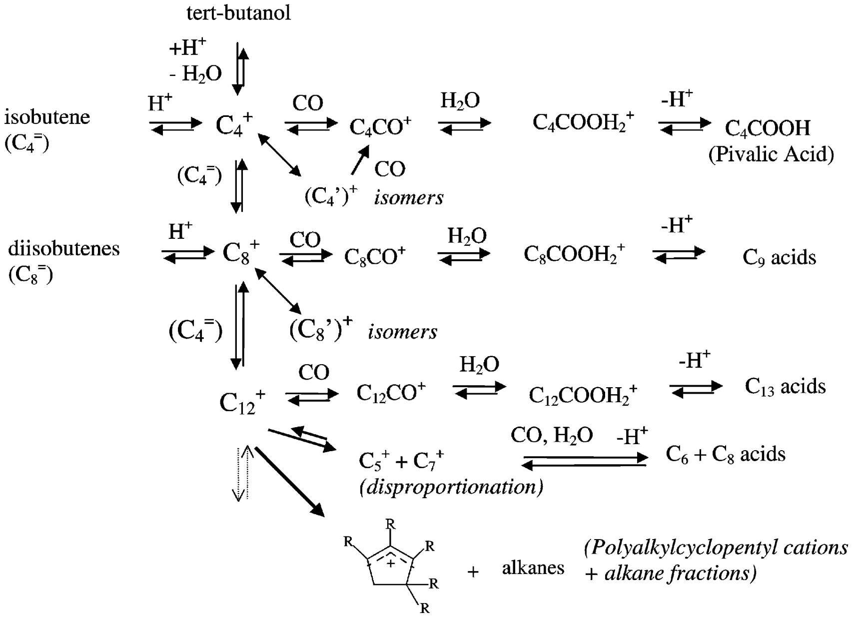

Fig. 1. (Simplified) Scheme of competing reactions in the Koch synthesis of pivalic acid.

Using the log–linear relationship found for $k_{1,\mathrm{app}}$ vs. Ho the protonation rate constants $k_{1,\mathrm{app}}$ at 96 wt.% H_2SO_4 can be estimated to be 3 (s^{-1}) for *tert*-butanol and approximately 10^{10} (s^{-1}) (thus a more or less instantaneous reaction) for isobutene. Under these conditions the protonation reaction rate is not likely to be rate determining. The reaction rate for the carbonylation step may be estimated from experimental data for the carbonylation reaction of the *tert*-butyl cation in superacidic media ($k_{\mathrm{carbonylation}} \approx 1.0$ (m^3/mol s), see [5]).

An overview of the most important competing reactions is presented in Fig. 1. Most byproducts are due to oligomerization and consecutive reactions including isomerization, disproportionation and carbonylation (leading to higher acids). At acid concentrations exceeding 90 wt.% stable polyalkyl-cyclopentyl (PACP) cations may be formed irreversibly [6]. Unfortunately, the kinetics for these side reactions are not known.

From Fig. 1 it can be concluded that at high dehydration rates of *tert*-butanol (or high protonation rates of isobutene) transport of CO to the reaction zone and mixing to avoid locally high alkene ($C_4{}^{2-}$) concentrations are essential. Attention will therefore be focused on these topics, together with the effect of adding an immiscible, inert, liquid to the reaction system.

3. Experimental work

For the experiments a high pressure autoclave was used, operated in batch or semi-batch mode. Experimental procedures to measure CO-consumption rates and the gas–liquid volumetric mass transfer coefficient k_La have been described elsewhere [1]. The experimental setup is shown schematically in Fig. 2. When the injection vessel is used for feeding the hydrocarbon reactant, it was filled with the liquid phase reactant, in most experiments a mixture of *tert*-butanol containing 8 wt.% of heptane to keep the *tert*-butanol in the liquid phase at 293 K.

After saturating the catalyst solution with CO, stirring was stopped and the reactor pressure was reduced by 1.5 bar by opening the valve to the (initially 30 bar CO containing) dump vessel. In this way a pressure drop over the injection vessel is created. Then the gas-inducing stirrer is started again. Both valves of the injection vessel are opened and the CO flow is used to inject the reactant. The relevant pressures and temperatures (indicated in Fig. 2) are recorded. The CO pressure in the reactor is kept constant by the pressure reducer or a pressure regulating system (±0.01 bar), consisting of a PC + PID controller. Data acquisition is stopped when no longer CO is consumed, minimally after 45 min. In the experiments with the reactant injector, the reactor is kept at 40 bar CO partial pressure and the injection time could be varied separately. The minimum injection time for a 13 ml of *tert*-butanol/heptane solution (containing ca. 9.5 g of *tert*-butanol) is approximately 16 s in the set-up used.

From the pressurized reactor a sample of about 100 g from the reaction mixture is directly quenched (at 10 bar CO) on 200 g of ice-water under stirring. The sample of the quenched reaction mixture was extracted in four steps with about 60 g heptane (99.9%, Merck, pro analyses). The organic layer was analyzed

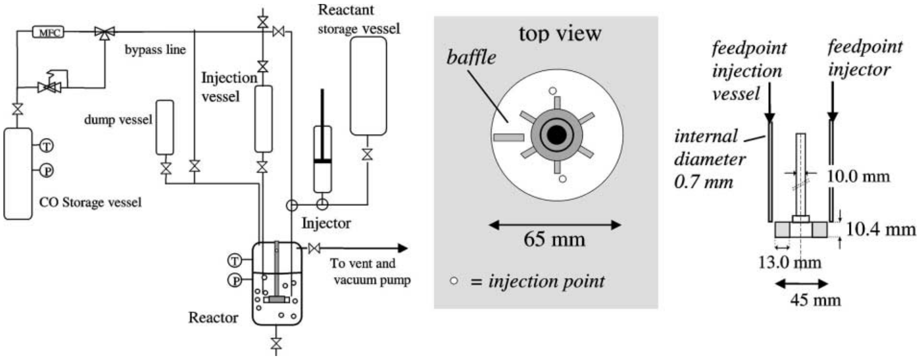

Fig. 2. Experimental setup.

by gas chromatography using a Varian 3400 GC (FID detector, 523 K, DB-FFAP column 30 m × 0.258 mm, 0.25 μm film, split injection, He or N_2 as carrier gas). The organic layer was also titrated to determine the total concentration of weak acids. Also, the consumption of CO during the reaction was recorded and used for calculating the total amount of CO containing products (acids) formed. The analyses of the organic layer retrieved after extraction on the total amount of acids using GC and titration are in good agreement.

In two experiments 5 g of pivalic acid was added to 380 g, 96 wt.% H_2SO_4 catalyst solution at 5 and 40 bar CO, respectively. After 1 h samples were taken to determine to what extent retro-Koch reactions have occurred. In these experiments a negligible amount of higher acids was detected. The higher acids found in the reaction product are therefore not formed by a retro-Koch reaction of pivalic acid under the conditions used in this study! The stability of C_9 acids was tested in a separate run in which 18.4 g of a mixture of C_9 acids was injected at 293 K and 40 bar CO in 380 g, 96 wt.% of sulfuric acid catalyst solution. After 6 h a reactor sample was taken and it was found by GC analysis that only 1.8% of the injected C_9 acids was converted to pivalic acid. No other acids than C_9 acids and pivalic acid were found. For the product analysis by GC two yield parameters are defined. The parameter Y_A is the yield on carboxylic acids on a molar basis; Y_A = mole of acid formed per mole reactant used (*tert*-butanol or isobutene). The carbon yield parameter Y_C is defined as follows: $Y_C(C_x) = xY_A(C_x)/(x-1)\,4$, the factor 4 in the above equation originates from the C_4 reactants used $Y_C(C_x)$ now represents the carbon atom yield on C_x acids based on the total amount of injected carbon atoms as hydrocarbon. Note that for the production of, e.g. a C_9 acid exact two C_4 reactant molecules are required. Since attention is focused on the total acid yield and the selectivity towards the primary product pivalic acid at different process conditions, higher acids formed were not analyzed for isomers.

4. Results

Subsequently the effects of the reactant feed rate, stirring rate and the presence of an immiscible liquid phase on the total acid yield and on the product distribution will be presented.

From Fig. 3 it can be seen that the injection rate has a very strong effect on the acid yield and on the product composition obtained. The acid yield for the *tert*-butanol experiments using the injection vessel seems somewhat higher than for the *tert*-butanol experiments using the injector at the same feed rate. Possibly, this difference can partially be attributed to CO dissolved in the reactant solution when using the injection vessel, since in the latter technique CO is used to inject the reactant solution, see Fig. 2, and (partial) saturation of this solution with CO is unavoidable. Alternatively, there could be a difference in the

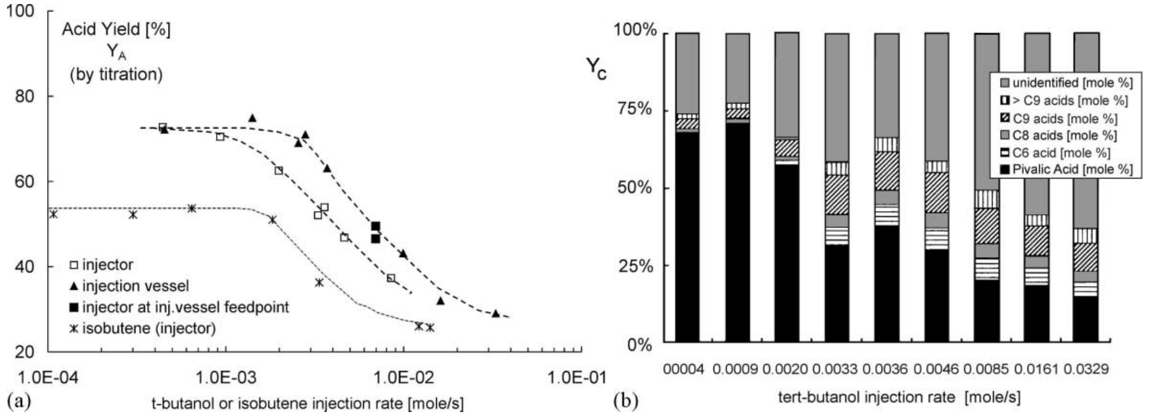

Fig. 3. (a and b) Effect of the hydrocarbon injection rate on acid yield Y_A and product composition Y_C. Conditions: 9 g of reactant, 40 bar CO, 293 K, 380 g of 96 wt.% H_2SO_4, 1800 rpm.

Table 1
Effect of stirrer speed on acid yield Y_A (by titration) and product composition Y_C (by GC analysis)

Stirrer speed N (rpm)	k_La (s^{-1})	High injection rate (0.025 mol/s)					Low injection rate (0.0009 mol/s)				
		Y_A (%)	Y_C:C_5 (%)	C_6+C_8 (%)	C_9 (%)	>C_9 (%)	Y_A (%)	Y_C:C_5 (%)	C_6+C_8 (%)	C_9 (%)	>C_9 (%)
800	0.08	25	11	7	5	2	66	39	12	14	6
1050	0.10	30	10	9	5	4	82	72	3	5	4
1400	0.12	34	11	9	9	6	83	68	2	4	2
1800	0.15	41	18	10	10	4	83	71	1	3	2

mixing (local energy dissipation rate) around the feed inlet points. This was tested by connecting the injector to the feedpipe of the injection vessel. The results indicate that indeed the feedposition is important, see Fig. 3.

At lower feed rates the formation of oligomers seems to be suppressed and the selectivity to pivalic acid increases. The 'unidentified products' in Fig. 3b involve a.o. acid soluble PACP cations and accompanying alkane fractions [6], judging by the position in the GC diagram and the UV-absorption at 292 nm. Additionally, acid soluble components like alkylsulfates may be formed.

The effect of the stirrer speed on product yield at high and low injection rates is presented in Table 1. The feed rate varied slightly within this series. Although the acid yield increased significantly with the stirrer speed, the acid product composition remained essentially constant. Only the formation of the PACP cations seemed to be suppressed more effectively at higher stirrer speeds. However, in these experiments the effect of CO transport and mixing cannot be separated completely, since a gas-inducing stirrer was applied. At low injection rates the acid yield was essentially constant but now the selectivity towards pivalic acid increases and to higher acids decreases with mixing intensity (stirrer speed).

Industrially, the process is usually operated as gas–liquid–liquid reaction system. The presence of a second liquid phase may have some influence on the mixing and especially on the CO transport towards the reaction zone. The role of such a dispersed liquid phase on the product distribution has been studied in this reaction system by taking heptane as immiscible organic liquid phase. The volumetric CO solubility is approximately 3.5 times higher in heptane than in the catalyst solution. To check the inertness of heptane, in one experiment no reactant but only heptane was injected. It was found that no CO was consumed due to a reaction and no products were found. In Fig. 4a

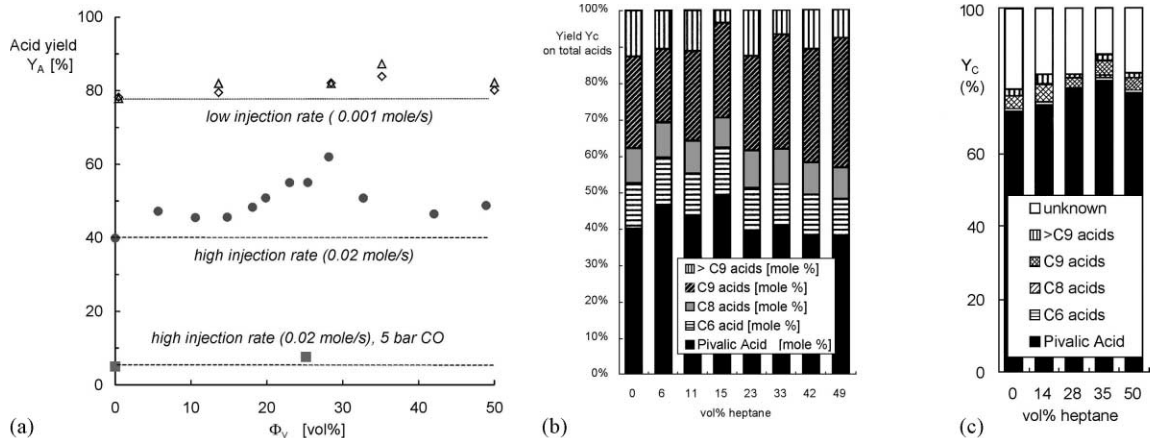

Fig. 4. (a–c) Effect of an immiscible heptane phase on the acid yield Y_A for *tert*-butanol injection vessel, 9 g of *tert*-butanol, 380 g 96 wt.% H_2SO_4, 1800 rpm, 40 bar CO, 293 K.

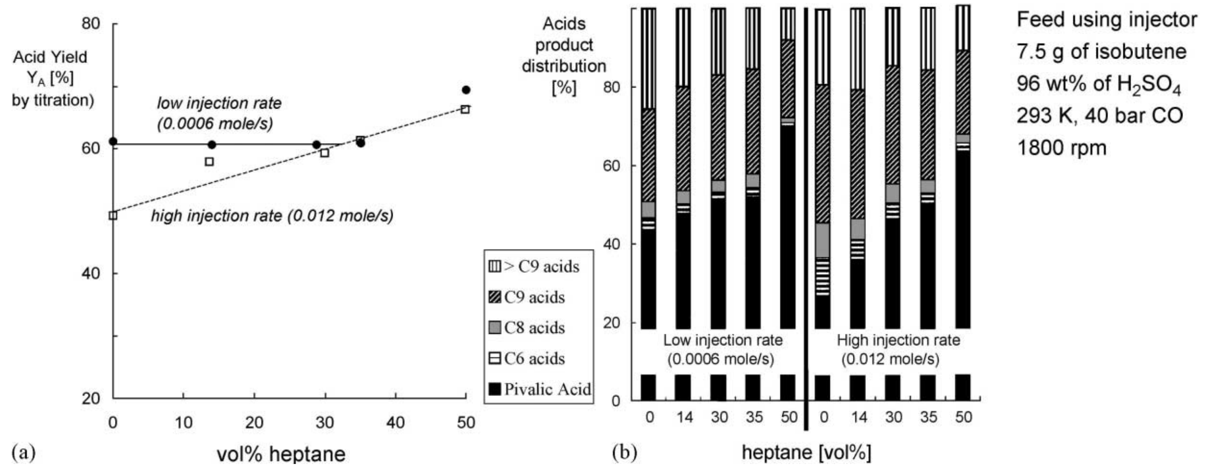

Fig. 5. (a and b) Effect of inert heptane phase on acid yield and acid product distribution for isobutene.

the results at different holdups of heptane initially present in the reactor are shown for *tert*-butanol experiments at 1800 rpm and a relatively high injection rate. From Fig. 4a an increase in the acid yield can be observed within the range of 0–30 vol.% heptane. At higher holdup this increase stops and even a decrease is observed, probably caused by phase inversion phenomena or a decreased mixing intensity. The product composition for the detected carboxylic acids seems not to be significantly influenced by the heptane phase, see Fig. 4b. In two experiments at 5 bar CO it was found that on addition of 25 vol.% of heptane the yield increased with 50% from 5 to 7.5%. These acid yields, when comparing to the 40 bar experiments, are almost in proportion to the decrease in CO pressure, indicating that the yield is limited by the CO solubility and CO transport. For a similar series at low *tert*-butanol injection rates (<0.001 mol/s) a similar increase in the acid yield with increasing heptane holdup was observed, as well as an increase in the selectivity towards pivalic acid (Fig. 4c). The increase in yield was even more pronounced in another set of experiments at 800 rpm.

For isobutene again a small effect in acid yield at low injection rates and a stronger increase at higher injection rates was observed, see Fig. 5. Surprisingly, at 50 vol.% of heptane the yield increased significantly. In this case phase inversion appears to be beneficial in preventing a reaction locus near the feed inlet; isobutene may be more effectively distributed over the reactor. The selectivity towards pivalic acid increases with the heptane content, even for the low injection rate series (see l.h.s. of Fig. 5b).

5. Discussion

From the results above it appears that the presence of CO in the reaction zone is a key factor. The solubility of CO in the sulfuric acid catalyst solution has been determined experimentally and was found to be 1.5×10^2 mol/m^3 at 40 bar CO and 293 K. For a CO-saturated catalyst solution and 9 g of *tert*-butanol as reactant this implies that the amount of CO dissolved in the catalyst is sufficient for the production of about 25% acid yield, which is in accordance with the results in Fig. 3a. For higher yields the amount of CO introduced via the reactant solution (when using the injection vessel) and the rate of gas–liquid mass transfer should be considered.

The apparent gas–liquid mass transfer rate can be determined from the rate of relative saturation of the catalyst solution with CO. The $k_\mathrm{L}a$ values thus calculated for the sulfuric acid/heptane dispersions increased slightly with the heptane volume fraction from 0.15 s^{-1} at zero heptane holdup to 0.25 s^{-1} at 30 vol.% (and higher) of heptane (all data at 1800 rpm). Considering, that the CO capacity of the dispersion increases with the heptane volume fraction, the gas absorption rate is even stronger affected if the mass transfer path is gas → catalyst phase → heptane. This implies that, e.g. for the experiment at 50 vol.% heptane the maximum CO mass transfer rate is approximately three times the mass transfer rate at 0 vol.% heptane!

The importance of the reactant feed rate was clearly illustrated in Fig. 3a. The observed trend will be determined by the CO transport rate and the CO consumption rate. Using the $k_\mathrm{L}a$ values determined the maximum CO mass transfer rate for the conditions of Fig. 3 can be estimated to be approximately 5×10^{-3} mol/s, which is approximately at the inflection point of the curve. At high injection rates the CO mass transfer rate in the agitated reactor is insufficient to keep the catalyst solution saturated. As the yield curve levels off at high injection rates, the reaction kinetics for both the carbonylation reaction and the oligomerization/isomerization side reactions must be faster than the gas–liquid mass transfer rate.

At low injection rates the CO transport from the gas phase to the bulk of the catalyst solution is sufficiently large. Macroscopically, the catalyst solution will be saturated with CO at all times. However, locally around the feedpoint still some CO depletion will occur and in addition micromixing effects may dominate the final acid yield obtained. Also the difference in the acid yield under identical operating conditions using isobutene as reactant when compared to using *tert*-butanol may be caused by this local depletion effect. This is further supported by the experiments with the exchanged feedpoints (Fig. 3a and b) and the effect of stirrer speed at low injection rates (Table 1). Further evidence was obtained by diluting a *tert*-butanol reactant solution at identical feed injection rates (moles of *tert*-butanol injected per unit of time). Going from 10 molar *tert*-butanol reactant to a 3 M solution (in heptane) the acid yield increased from 65 to 75%. This effect may be partly due to a decreased reactant concentration and partly to an increase in CO transported along with the reactant. Even stronger effects at dilution of the reactant are expected for isobutene, since in that case the reactant does not need to be dehydrated before oligomerization can take place. For practical reasons this type of experiment was not carried out.

In case heptane is present as an immiscible inert liquid phase, its main effect is a strong increase of the macroscopic gas–liquid mass transfer of CO (see $k_\mathrm{L}a$ values mentioned above and the results of Figs. 4a and 5a). The underlying mechanisms of this gas absorption rate enhancement must, however, still be clarified. In cases where the macroscopic gas–liquid mass transfer rate is sufficient, the presence of the inert, CO carrying, heptane drops can be beneficial in suppressing local CO-depletion, as suggested by the results in Figs. 4a and 5a for the low injection rate series. Liquid–liquid mass transfer around the feed point is likely to be faster than gas–liquid mass transfer due to the larger interfacial area.

With increasing holdup of heptane the initial present CO increases from an amount sufficient for 25% conversion of the injected *tert*-butanol to 100% conversion at 48 vol.% heptane for the experiments shown in Fig. 4a. The experimentally determined acid yield, however, did not go to completion. All series with increasing heptane holdup show an increase in the acid yield with increasing heptane volume fraction, which is less that the corresponding increase in CO capacity of the dispersion. Mixing and liquid–liquid mass transfer of CO is in the experiments with high volume fractions of heptane apparently not fast enough to ensure very high acid yields and the oligomerization reactions, including the PACP cation formation, must be extremely fast.

At very high holdups of the inert heptane phase, phase inversion phenomena may become important. Different effects were observed for *tert*-butanol and for isobutene as reactant. In case of isobutene as reactant the pivalic acid production seems to benefit from this phase inversion; most likely due to a better distribution of isobutene throughout the reactor before it reacts (instantaneously) in the now dispersed reactive sulfuric acid drops/zones. For *tert*-butanol this effect is almost the opposite; phase inversion does not lead to higher yields and even a decrease in yield was noticed. Possibly this must be attributed to the higher physical solubility of *tert*-butanol in the sulfuric acid phase, so that it cannot benefit completely from the distribution-effect through the continuous organic phase.

6. Concluding remarks

For the H_2SO_4 catalyzed production of pivalic acid from *tert*-butanol and isobutene the CO transport was found to be the major parameter determining the acid yield. Both the carbonylation reaction and the oligomerization reactions are fast with respect to gas–liquid and liquid–liquid mass transfer. The protonation of isobutene is much fast than the dehydration of *tert*-butanol in the 96 wt.% sulfuric acid catalyst solutions used. Especially for isobutene the CO transport to the reaction zone as well as the mixing intensity at the feed inlet are therefore very important. The presence of an immiscible organic liquid phase increased the acid yield and selectivity significantly by enhancing gas–liquid mass transfer and suppressing local CO depletion by liquid–liquid transfer. Phase inversion effects can be beneficial but deserve further study. The results obtained indicate that the current production methods should be reconsidered.

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