

# Acidic and basic ion exchange resins for industrial applications

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## Abstract

Ion exchange resins, particularly the macroporous variety, are very versatile catalysts, which play a more and more important role in the large scale manufacture of petrochemicals and solvents. Different acid and basic resins have been studied for several reactions in order to improve the catalytic performances and the process engineering with respect to current technology. Strongly basic resins were checked as catalysts for the methanol carbonylation to methyl formate. Strongly acid resins were instead employed in the isobutene dimerization to produce a mixture of ether and branched hydrocarbons, mainly C<sub>8</sub>, with high octane number. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The synthesis of organic ion exchangers, first reported in 1935 [1], made possible their use as heterogeneous acid base catalysts, thus opening a vast field of catalysis. Actually, ion exchange resins, particularly the macroporous variety, are very versatile catalysts, which offer several advantages over the homogeneous catalysts with respect to corrosion, pollution, product recovery and selectivity.

While basic resins have not yet found an industrial application, primarily as a result of their low stability at temperature higher than 50°C, acid resins are well established catalysts in the large scale manufacture of chemicals. These resins are employed for the production of isopropyl alcohol (IPA) by propylene hydration, of methyl isobutyl ketone (MIBK)

from acetone [2], and mainly in the synthesis of methyl tertiary-butyl ether (MTBE) by etherification of isobutene with methanol.

In this framework, two new possible application fields of resins as catalysts (isobutene dimerization and methanol carbonylation) are reported here. Isobutene dimerization is a powerful alternative to MTBE production whenever use of the latter will be forbidden in gasoline, as for example in California, while methanol carbonylation to methyl formate is an example of resins application in basic catalysis in order to improve the current technology based on the sodium methoxide homogeneous catalysts. In this paper a few unreported particular aspects of these two applications are pointed out.

## 2. Experimental

Experimental procedures are described in other papers; for methanol carbonylation see [3], for isobutene dimerization see [4].

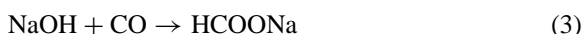
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### 3. Methanol carbonylation to methyl formate

Methyl formate represents an interesting product by itself and a valuable intermediate for the production of other chemicals such as formic acid, formamide, and *N,N*-dimethylformamide. Methanol carbonylation to methyl formate is an exothermic equilibrium limited reaction, industrially carried out in homogeneous liquid phase using sodium methoxide as catalyst at the temperature of 80°C and CO pressure of 4.5 MPa. About 95% of CO and 30% of methanol are converted under plant conditions, but nearly quantitative conversion of methanol can be achieved by recycling the unreacted alcohol [5].



The most significant drawback of the current industrial process is represented by a progressive deactivation of the methoxide due to the presence of traces of water and CO<sub>2</sub> in the feed. These poisons cause its transformation into weaker bases: sodium formate (reactions 2 and 3) and sodium methoxycarbonate (reaction 4), both of which are insoluble in the reaction medium and cause clogging, fouling as well as catalyst loss.

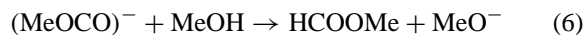
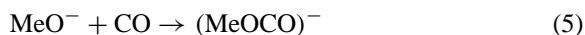


Therefore, the use of a heterogeneous catalyst for this particular reaction should be very attractive in order to avoid solubility and plugging problems and, above all, in order to ease the recovering and reactivation of the deactivated catalyst from methanolic solutions of methyl formate. In a preliminary study [3] we

reported the influence of the characteristics of different resins in terms of crosslinking, morphology and nature of functional groups. In this context, we tested catalytic performance of several basic resins differing in the polymer matrix (polystyrene or polyacrylates) and quantity of functional groups (Table 1) and compared them with the sodium methoxide homogeneous catalyst. Each resin was carefully activated to assure a complete exchange of Cl<sup>-</sup> anions with the OH<sup>-</sup> and subsequently with the CH<sub>3</sub>O<sup>-</sup> groups, which are the effective catalytic species.

As reported in Fig. 1, macroporous resins displayed a very interesting behavior in the preliminary batch tests. Amberlyst A26 provided the most active catalyst with a high activity also at temperature as low as 55°C, at which the homogeneous catalyst is low-effective and the thermodynamic equilibrium is favorable for product. IRA 958 showed insufficient activity owing to the small concentration of basic sites in the resin beads.

Afterwards, the effect of Amberlyst A26 concentration was evaluated and compared with that of sodium methoxide. As shown in Fig. 2, the reaction rate increases with catalyst concentration but the correlation is not linear and a tendency towards the zero reaction order was observed on increasing the catalyst concentration. This behavior is in accordance with the two-step reaction mechanism proposed for the homogeneous system [6].



First, the alcoholate ion interacts with carbon monoxide to form a complex (reaction 5) which later on reacts with methanol to regenerate the active catalyst and to produce methyl formate (reaction 6). The rate determining step of the overall reaction is the

Table 1  
Characteristics of ion exchange resins (macroporous)<sup>a</sup>

Resin	Type	Matrix structure	Functional group	Declared exchange capacity (meq/g)	Max. operating temperature(°C)
Amberlyst A26	Basic	Styrene-DVB	-N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	4.4	60 (OH <sup>-</sup> form)
IRA 958	Basic	Acrylic-DVB	-N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	2.6	40 (OH <sup>-</sup> form)
Amberlyst 15	Acid	Styrene-DVB	-SO <sub>3</sub> H	4.8	120
Amberlyst 35	Acid	Styrene-DVB	-SO <sub>3</sub> H	5.2	120

<sup>a</sup> All furnished by Rohm & Haas.

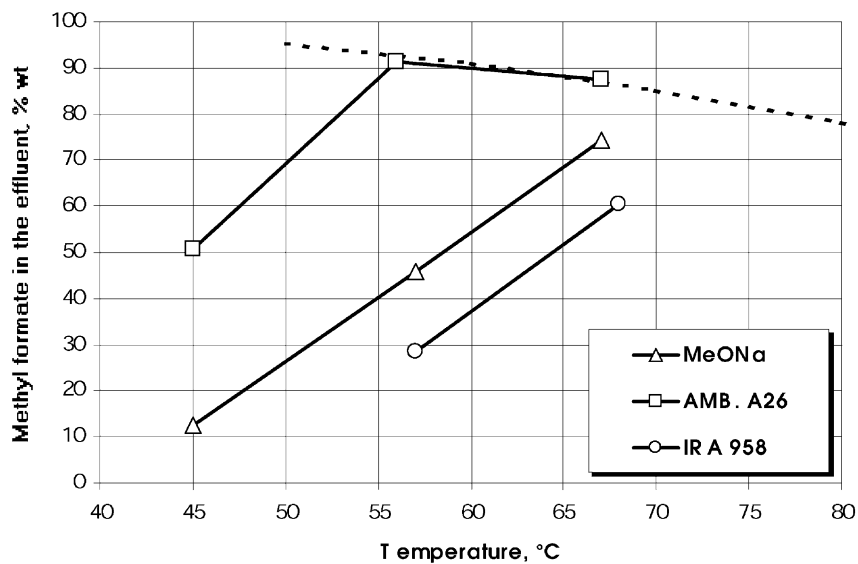


Fig. 1. Methanol carbonylation — screening of homogeneous and resin catalysts in batch runs. Reaction conditions: time, 3 h; CO pressure, 5 MPa; alcohol/base molar ratio  $\approx 200$ . The dotted line depicts the thermodynamic equilibrium according to reference [5].

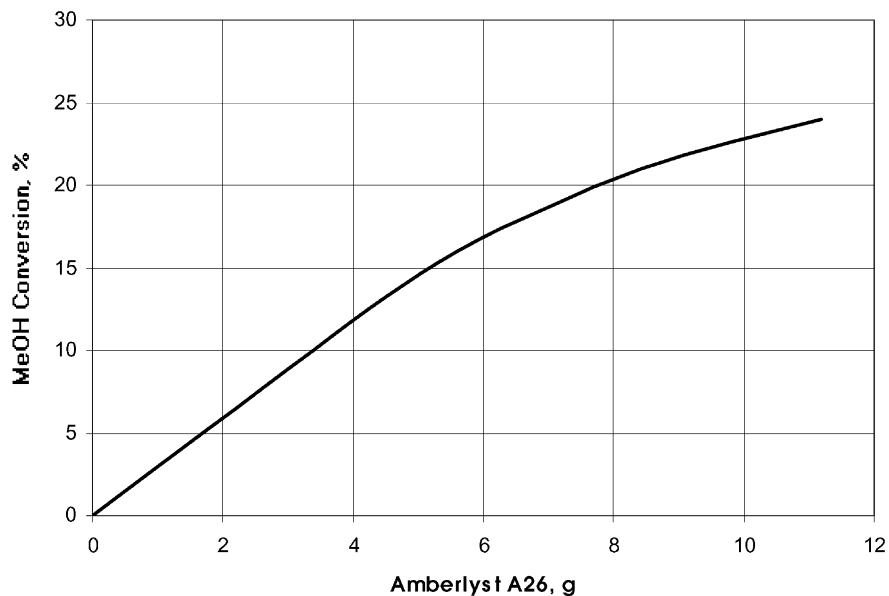


Fig. 2. Methanol carbonylation with Amberlyst A26 catalyst — effect of catalyst concentration. Reaction conditions: time, 1.5 h; CO pressure, 5 MPa;  $T$ , 52°C.

reaction 5 when the concentration of catalyst is low, the reaction 6 controls the overall rate at higher catalyst concentrations.

In order to obtain a deeper insight into the temperature stability of Amberlyst A26 and its resistance towards poisons such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , methanol carbonylation was also studied by means of continuous runs. In these tests, methanol was continuously fed to the reactor and the reaction mixtures containing methanol and methyl formate were removed at the same rate, thus maintaining a nearly constant liquid phase volume in the reactor.

Continuous runs aimed at testing the catalyst deactivation were carried out at temperature of  $48^\circ\text{C}$ . As shown in Fig. 3, the concentration of methyl formate initially increases because the reaction rate is faster than the feeding rate. At longer reaction times, methyl formate concentration decreases due to deactivation effects. The resin activity can be completely restored by its regeneration with caustic washing showing that only reversible catalyst deactivation takes place.

In order to check thermally induced deactivation processes, another set of runs was carried out at higher temperature ( $67^\circ\text{C}$ ) with the same sample of Amberlyst A26, which was regenerated after each

cycle (Fig. 4). Also under these adopted conditions, the resin catalytic activity could be completely restored by the caustic washing regeneration, as pointed out from virtually constant maximum activity achieved in all runs. Small deviation observed in the third run is probably due to an accidentally higher level of poisons in the methanol fed.

These results show that only reversible catalyst deactivation occurs even at  $67^\circ\text{C}$ , which is surprising because this type of resin is claimed to be unstable in the  $\text{OH}^-$  formed at temperatures higher than  $60^\circ\text{C}$  (the maximum operating temperature reported by the resin producer), due to a loss of the ionic structure as a consequence of the Hofmann degradation. Surprising thermal stability of the active group (also observed at  $70^\circ\text{C}$ ) can be explained by the presence of  $\text{MeO}^-$  instead of  $\text{OH}^-$  counter-anions.  $\text{MeO}^-$  ions could inhibit the irreversible deactivation mechanism, thus enhancing the thermal stability of the Amberlyst A26 resin.

These preliminary results show that Amberlyst A26 seems to be a very attractive catalyst for methanol carbonylation but in order to make possible an industrial application at least longer lifetime tests have to be accomplished.

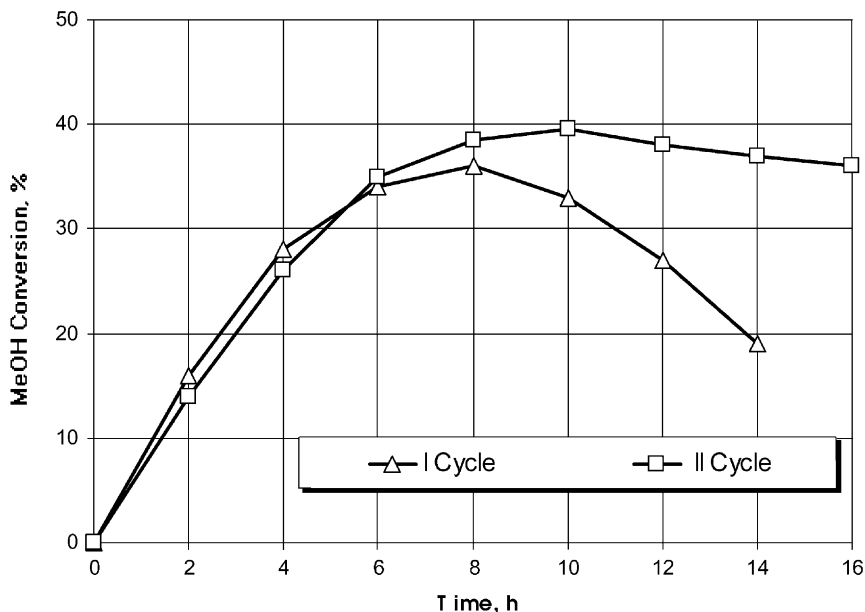


Fig. 3. Methanol carbonylation with Amberlyst A26 catalyst — reversible deactivation in continuous runs. Reaction conditions: liquid hour space velocity (LHSV),  $2\text{ h}^{-1}$ ; CO pressure, 5 MPa;  $T$ ,  $48^\circ\text{C}$ .

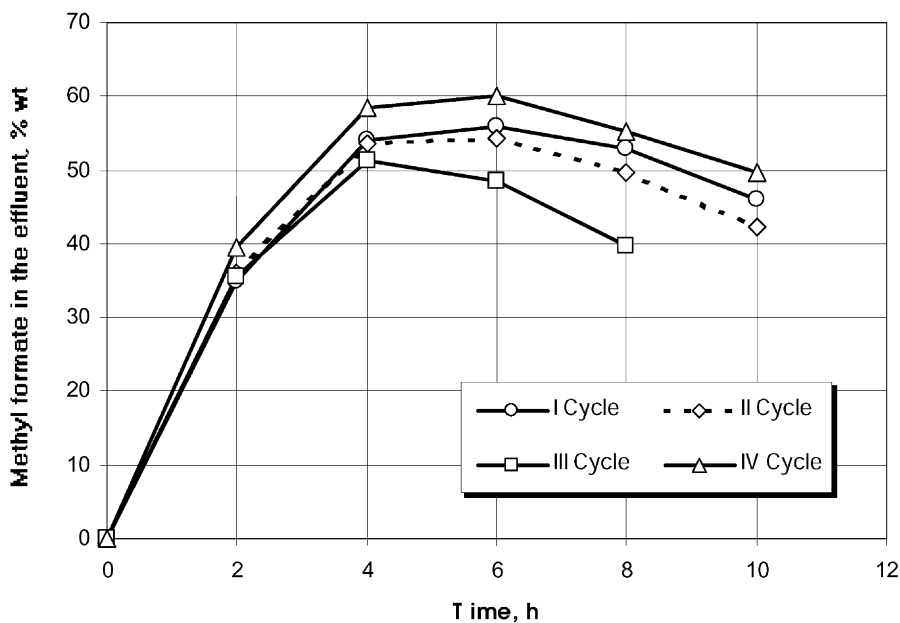


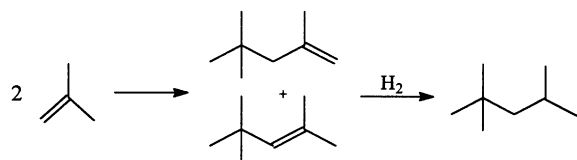
Fig. 4. Methanol carbonylation with Amberlyst A26 catalyst — reversible deactivation in continuous runs. Reaction conditions: LHSV,  $2\text{ h}^{-1}$ ; CO pressure, 5 MPa;  $T$ ,  $67^\circ\text{C}$ .

#### 4. Isobutene dimerization

Branched saturated hydrocarbons formed in the isobutene dimerization represent a very important class of compounds for gasoline reformulation. Isobutene dimerization may be carried out in the liquid phase with acid catalysts but, so far, this reaction has found only a few industrial applications [7].

2,4,4-Trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene are the main isobutene dimers produced with acid catalysis. These low volatile olefins can be easily hydrogenated to isooctane (2,2,4-trimethylpentane) which is the reference compound for rating the gasoline antiknock properties (octane numbers: RON = MON = 100 (Scheme 1)).

Acid ion exchange resins, such as Amberlyst 15 and Amberlyst 35 produced by Rohm & Haas



Scheme 1. Isobutene to isooctane.

(styrene-divinylbenzene copolymers with sulphonic groups as the functional structure) are the most suitable catalysts (Table 1).

The most important problem of isobutene dimerization is the control of the reaction rate (isobutene oligomerizes very quickly) in order to prevent formation of larger amounts of higher oligomers (about 20–25% of trimers and more than 2% of tetramers). Tetramers fall outside the gasoline boiling range and, as regards trimers, such a huge percentage of high boiling compounds is not acceptable in “Cleaner Burning Gasolines”.

Preliminary tests were carried out in the liquid phase operating with a water cooled bench reactor (Table 2); the results achieved are in a good agreement with previously reported data [7,8] and display a very high formation of heavy species.

Product quality may be significantly improved by introducing an alcohol (methanol, ethanol or higher) with ROH/isobutene molar ratio lower than 1 in the reacting system. Alcohol lowers the reaction rate but increases the reaction selectivity of dimers to 85–90% and decreases the content of tetramers to a few hundred parts per million. Since the alcohol is fed to the system some ether is produced (MTBE if the alcohol

Table 2  
Isobutene dimerization<sup>a</sup>

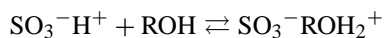
	a	b	c
Isobutene conversion (%)	85.6	58	up to 99%
Product composition (%)			
C <sub>8</sub>	54.2	52	58.0
C <sub>12</sub>	40	40	38.3
C <sub>16</sub>	5.8	8	3.7

<sup>a</sup> Product composition. (a) Isobutene, 53 wt.%; Amberlyst 15, *T*, 40–100°C, LHSV, 5.5 h<sup>-1</sup> [4]; (b) Isobutene, 30% wt.; Amberlyst 15, *T*, 60°C; LHSV, 1 h<sup>-1</sup> [8]; Isobutene, 45.4% wt.; catalyst: acid slurry, *T*, 100°C [7].

is methanol, ETBE if the alcohol is ethanol) and, as a consequence, the final product will be a mixture of oligomers (dimers and trimers) and ether. Exact composition of the product depends on the alcohol/isobutene molar ratio fed as shown in Fig. 5 for the case of ethanol.

The effect of the concentration of acid sites on the resin is very important for isobutene dimerization: under similar space velocity, temperature and reactants concentration conditions, the most acidic Amberlyst 35 (5.2 meqH<sup>+</sup>/g) resulted more active than Amberlyst 15 (4.8 meqH<sup>+</sup>/g), giving isobutene conversion 5–10% higher [4].

Different alcohols (methanol, ethanol and higher) were tested in this reaction. It was observed that the different nature of the alcohols influences the reaction rate of the isobutene dimerization process; due to its high polarity, the alcohol is preferentially adsorbed on the active sites of the catalyst according to the following reaction:



The presence of the alcohol reduces the strength of the acid sites and, as a result, the rate of the oligomerization reactions is much reduced and the selectivity to dimers is increased.

This effect is typical not only in case of methanol but also in that of higher alcohols; very attractive results were achieved with ethanol and as well as isopropanol which form ethers (ETBE and IPTBE), which have very high octane numbers. The thermodynamic equilibrium for the etherification reaction is less favored for these higher alcohols and as a consequence there is more free alcohol in the system. This fact causes further reduction of the acid strength and, as a result, isobutene conversion decreases and selectivity to dimers increases as shown in Fig. 6.

Other experiments, reported in Fig. 7, showed that for alcohols higher than isopropanol, such as

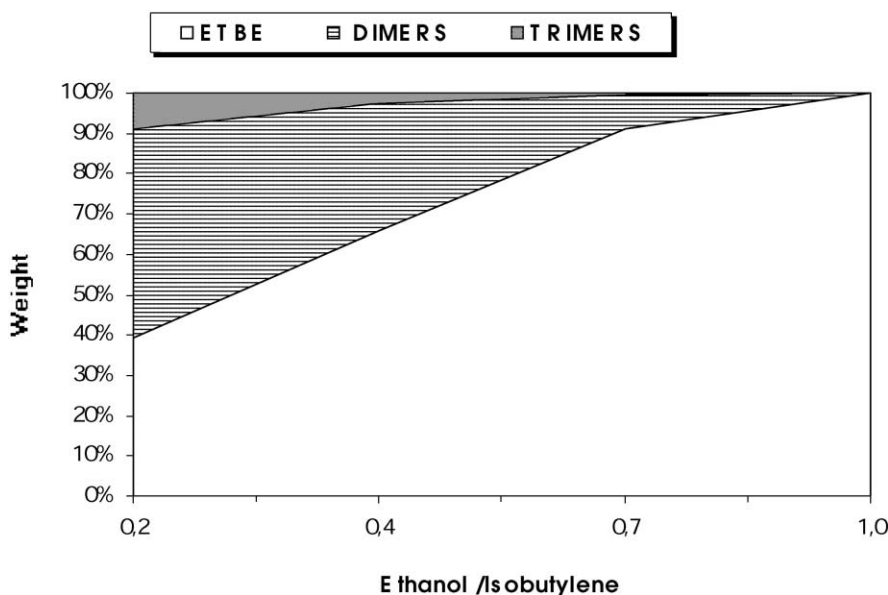


Fig. 5. Isobutene dimerization in the presence of ethanol with Amberlyst 35 catalyst — product composition.

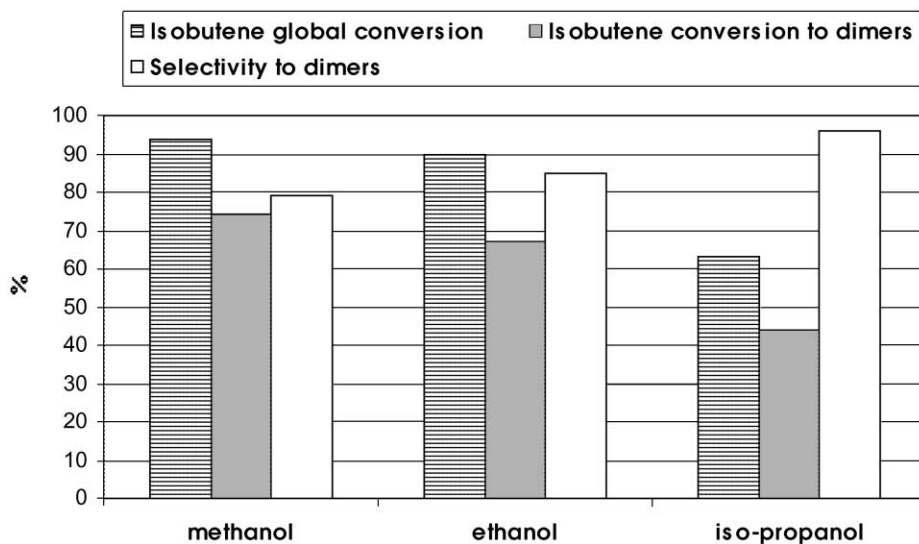


Fig. 6. Isobutene dimerization with Amberlyst 35 catalyst — alcohol effect. Reaction conditions: time, 3 h; alcohol/isobutene molar ratio, 0.2; isobutene in C<sub>4</sub> feed, 45–50%; T of water, 40°C (50°C for iso-propanol); LHSV, 4.6 h<sup>-1</sup>.

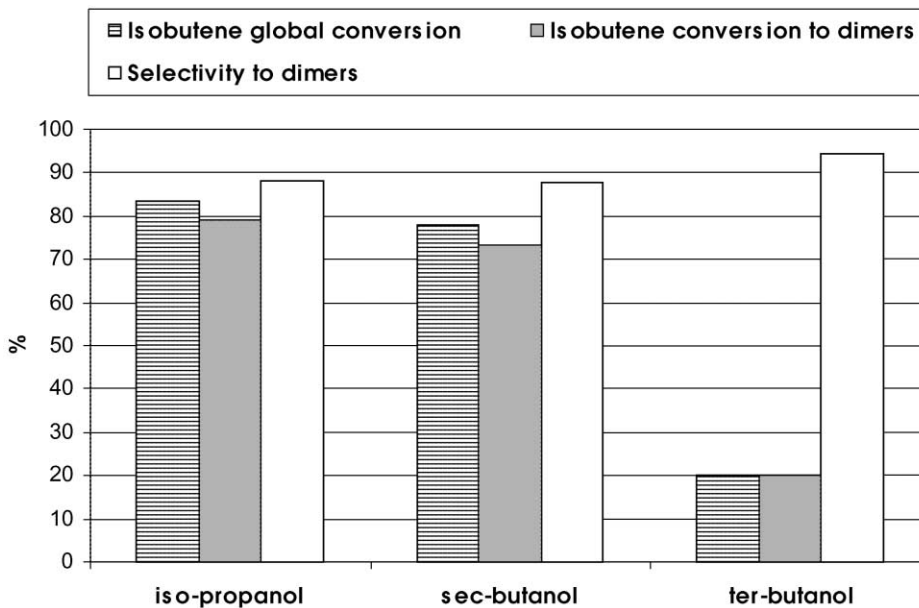


Fig. 7. Isobutene dimerization with Amberlyst 35 catalyst — alcohol effect. Reaction conditions: time, 3 h; alcohol/isobutene molar ratio, 0.05; isobutene in C<sub>4</sub> feed, 45–50%; T of water, 40°C (50°C for TBA); LHSV, 4.6 h<sup>-1</sup>.

secondary-butanol, the differences of reaction rate are very low and using very small alcohol/isobutene molar ratio (0.05) it is possible to obtain good isobutene conversion to dimers still with very high selectivity. Finally when tertiary alcohols, such as tertiary-butanol, are employed, no ether is formed due to steric hindrance and pure dimerization is achieved. In this case, however, the alcohol is in equilibrium with water, through the dehydration reaction of isobutene and water, and the latter is strongly adsorbed on the active sites, thus further reducing acid strength and making dimerization reaction rate very low although selectivity is very high.

## 5. Conclusion

In this work we have shown that new attractive technologies can be designed by using ion exchange resins as catalysts. On the basis of the obtained results the following concluding remarks can be drawn.

1. The use of strongly basic resins, as Amberlyst A26, appears as a valuable tool for significantly improving the current industrial process of methyl formate production. These heterogeneous systems allow to reach the equilibrium concentrations in a shorter reaction time and at lower reaction temperatures (50–70°C) compared to sodium methoxide, the industrial homogeneous catalysts. Recycling experiments have shown that the catalyst maintains its activity after several cycles also at temperature as high as 67°C (reversible deactivation).
2. Strongly acid resin, as Amberlyst 35, can be used without any problem for the isobutene dimerization. As a result, a new technology has been developed that has already been tested on the industrial scale in different MTBE plants [9].

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