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MTBE and alkylate co-production: fundamentals and operating experience

Marco Di Girolamo*, Lorenzo Tagliabue

Snamprogetti SpA, Research Laboratories, Via Maritano 26, 20097, S.Donato Milanese, Italy

Abstract

MTBE and mixtures of branched C_8 hydrocarbons with gasoline blending properties similar to alkylate can be produced in a wide range of relative ratios and in an environmentally-friendly way by the simultaneous isobutene etherification/dimerization reaction. In the present paper thermodynamics and kinetics of the MTBE synthesis are presented as the theoretical background before discussing the experimental results for the new process obtained at laboratory scale, on pilot plant and on an industrial unit. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: MTBE; Alkylate co-production; Etherification reaction; Dimerization reaction

1. Introduction

The worldwide trend for gasoline reformulation is toward lower evaporative emissions and a more complete combustion by means of [1]:

- an important and expanding role of oxygenates and branched saturated hydrocarbons (such as those found in alkylate) as gasoline components;
- a reduction of gasoline volatility, aromatics, lighter olefins and sulphur contents.

In this scenario, branched saturated hydrocarbons, made either by alkylation or by olefins dimerization and *tert*-alkyl ethers (MTBE, ETBE, TAME, etc.), come out as the two most important classes of compounds for the gasoline reformulation.

Alkylation is a well established process. However, a number of environmental concerns will cause increasing troubles for new plants based on the present technologies: HF should be ruled out for installations in populated areas due to its extreme toxicity, while H_2SO_4 is highly corrosive and produces great amounts of acid muds difficult to dispose of. Nevertheless, alkylate is particularly suitable for its high-octane number, the low volatility and the absence of sulphur and aromatics, so alternative processes with solid acid catalysts are being developed, though their commercial applicability still has to be proved [2]. Furthermore, in refineries, the alkylate availability is intrinsically limited upstream by the characteristics of the fluid catalytic cracking (FCC) unit thus resulting in a limited contribution to the reformulated gasoline pool.

This case study describes the evolution of the MTBE technology towards a process for the co-production of MTBE and high-octane branched C_8 hydrocarbons (mainly isooctane) through the simultaneous

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*Corresponding author. Tel.: +39-02-52046966; fax: +39-02-52056757
E-mail address: marco.digirolamo@snamprogetti.eni.it
(M.D. Girolamo)

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dimerization/etherification of isobutene. As this process, which requires only minor additions to a standard MTBE plant, yields an alkylate-like product in a cost-effective and environmentally-friendly way, it represents a new attractive alternative in the context of fuel reformulation.

Experimental results obtained on lab-scale reactor, pilot plant and an industrial unit are discussed. Kinetics and thermodynamics of the synthesis are also considered since their proper description is fundamental for the optimal design of the synthesis loop.

2. Background (MTBE synthesis)

2.1. Reaction

MTBE is produced by the liquid-phase addition of methanol to isobutene. The reaction is exothermic ($\Delta H_r = -9.5$ Kcal/mol) and is carried out over acidic ion-exchange resins. Suitable feedstocks are C_4 cuts containing isobutene; these are generally supplied by FCC, steam-crackers (SC) and isobutane dehydrogenation units (DHY).

Isobutene (IB) may vary from as low as 10–15% by weight in streams from FCC, up to 50–55% by weight in streams from DHY.

Since the reaction is exothermic and limited by the chemical equilibrium, in order to maximize the isobutene conversion, the reactor outlet temperature is maintained as low as allowed by the catalyst activity. Operating temperatures range between 40°C and 80°C.

Selectivity to MTBE is usually higher than 99%; the only by-products are diisobutenes (DIB), dimethylether (DME), *tert*-butyl alcohol (TBA), and if linear butenes are present, their corresponding ethers, mainly methyl-*sec*-butyl-ether (MSBE).

The overall reaction pattern is the following:

$$\mathrm{MeOH} + \mathrm{IB} \rightleftarrows \mathrm{MTBE} \tag{1}$$

$$2\mathrm{IB} \rightarrow \mathrm{DIB} \tag{2}$$

$$2\mathrm{MeOH} \rightarrow \mathrm{DME} + \mathrm{H_2O} \tag{3}$$

$$\mathrm{IB} + \mathrm{H_2O} \rightleftarrows \mathrm{TBA} \tag{4}$$

$$\mathrm{MeOH} + n\text{-butenes} \rightleftarrows \mathrm{MSBE} \tag{5}$$

Formation of both DIB and DME is thermodynamically favoured at synthesis conditions. However, unless the reactor is operated at high temperature and high contact time, this is limited to a few hundreds of ppms.

TBA formation is fast and approaches the thermodynamic equilibrium. However, it is limited by the small amount of water present inside the reactor. Water is an impurity both of methanol (specification is $H_2O<1000$ ppm) and of the C_4 feed (<500 ppm) and is formed at ppm levels along with DME in reaction (3).

The formation of by-products must be thoroughly monitored; rather severe specifications are imposed both on the ether quality (MTBE 98–99% min) and on the unreacted C_4 hydrocarbons since they may be further used as a feedstock for alkylation (in this case oxygenates such as MTBE, H_2O and DME must be completely removed as they increase the acid consumption).

Sulphonated poly(styrene-divinylbenzene) resins are the catalysts employed in the industrial practice for the MTBE synthesis. Standard products from different manufacturers (e.g. Rohm and Haas, Bayer, Purolite, Dow) have similar characteristics: the structure is of the macroporous type and the content of sulphonic acid groups is in the range 4.7–4.9 mmol H^+/g. In order to prevent deactivation by loss of sulphonic groups the suggested operating temperatures are lower than 120°C.

More active resins with more than 5 mmol H^+/g, e.g. Amberlyst 35 (Rohm and Haas), (5.3 mmol H^+/g) have been recently offered. These resins will takeover in the near future due to their superior catalytic properties [3].

2.2. Kinetics

As the MTBE synthesis occurs in a highly nonideal medium, kinetics is properly formulated in terms of the activities of the reacting species, a_i. It has been found that over a wide range of temperatures and reactants concentrations, the rate of formation of MTBE may be expressed as

$$r = \frac{k_1\, a_{\mathrm{IB}}\left(1 - \left(a_{\mathrm{MTBE}}/K_{\mathrm{eq},1} a_{\mathrm{IB}} a_{\mathrm{MeOH}}\right)\right)}{1 + \sum_i K_i (x_{i,\mathrm{p}} - x_i^*)},$$

where $K_{\mathrm{eq},1}$ is the equilibrium constant for the reaction, K_i are adsorption constants, x_i^* are molar fractions in the resin when the active sites are saturated with the species i, and $x_{i,\mathrm{p}}$ are the actual molar fractions in the resin.

This expression accounts for transitions of mechanism occurring on varying the relative concentrations among reactants. For instance, methanol saturates the catalytic sites when is present at high concentration since it is preferentially adsorbed with respect to the nonpolar C_4 hydrocarbons; in this case, the observed reaction order is zero or negative. On the contrary, when it is present in small concentration, since the number of catalytic sites occupied by methanol increases with its concentration in the liquid-phase, the observed reaction order is always positive. Both these situations are encountered in MTBE reactors as the methanol molar fraction along the bed length may vary from values as high as 0.3–0.4 to less than 0.01.

When the partition coefficients between the resin and the liquid-phase:

$$q_i = \frac{x_{i,\mathrm{p}}}{x_{i,\mathrm{l}}}$$

is approximated as a constant, the expression of the reaction rate may be conveniently rearranged in terms of the liquid-phase molar fractions, $x_{i,\mathrm{l}}$, as

$$r = \frac{k^* \, a_{\mathrm{IB}}(1 - (a_{\mathrm{MTBE}}/K_{\mathrm{eq}} a_{\mathrm{IB}} a_{\mathrm{MeOH}}))}{1 + \sum_i K_i^* x_{i,\mathrm{l}}}.$$

In this expression both the rate constant, k^*, and the adsorption constants K_i^* are adaptive parameters that incorporate the unknown quantities $x_{i,\mathrm{p}}$ and x_i^*.

2.3. Thermodynamics

As the MTBE reactors are designed to approach the thermodynamic equilibrium, the knowledge of the equilibrium conversion is fundamental for sizing an MTBE plant. The thermodynamic equilibrium for the MTBE is described by the following expressions:

$$K_{\mathrm{eq},1} = \prod_i a_i^{v_i} = \prod_i x_i^{v_i} \prod_i \gamma_i^{v_i} = \frac{x_{\mathrm{MTBE}}}{x_{\mathrm{IB}} x_{\mathrm{MeOH}}} \frac{\gamma_{\mathrm{MTBE}}}{\gamma_{\mathrm{IB}} \gamma_{\mathrm{MeOH}}} = K_x K_\gamma.$$

Since

$$x_i = \frac{n_i^0 + v_i \lambda_1}{\sum_i n_i^0 + \sum_i v_i \lambda_1}$$

once the feedstock composition (i.e. the moles of each species at t=0, n_i^0) and the equilibrium constant $K_{\mathrm{eq},1}=f(T)$ are known, the calculation of the equilibrium conversion proceeds by searching for the reaction extent, λ_1, which satisfies the nonlinear equation:

$$K_{\mathrm{eq},1} - K_x K_\gamma = 0.$$

It has been observed that the solution of this equation may be strongly affected by the method used to describe the liquid-phase nonideality; in fact, isobutene and MTBE behave almost ideally, i.e. $\gamma_i \cong 1$, therefore the equilibrium condition may be represented in the simplified form:

$$K_{\mathrm{eq},1} - \frac{K_x}{\gamma_{\mathrm{MeOH}}} = 0.$$

Under conditions of practical interest, the calculation of γ_{MeOH} may be critical; for instance, when the methanol concentration is small, i.e. <2–3% by weight, such as at reactor outlet conditions, different thermodynamic methods (e.g. UNIFAC, UNIFAC Dortmund, UNIFAC Lyngby, UNIQUAC, NRTL, Wilson) give results similar to those reported in Fig. 1.

Through tests carried out for a wide range of operating conditions (i.e. temperature, isobutene concentration, MeOH/isobutene molar ratio), it emerges that modified UNIFAC group contribution methods, both from Dortmund [4] and Lyngby [5], and Wilson method [6] describe accurately the isobutene equilibrium conversion, while other methods, e.g. UNIFAC [7], UNIQUAC [8] and NRTL [9], tend to underpredict it (Fig. 2). This behaviour is more pronounced the smaller the initial concentration of isobutene, i.e. the smaller the residual concentration of methanol [10].

2.4. Process description

So far, several companies have developed MTBE processes; these generally differ for the particular type of reactor used. Among the most diffused types are fixed-bed adiabatic reactors (ARCO, Phillips, IFP), catalytic distillation (CD Tech) and multitubular reactors (Snamprogetti). The scheme of a Snamprogetti High-Recovery MTBE plant is reported in Fig. 3.

In this type of plant, more than 99% of the isobutene is converted into MTBE by using two reactors with intermediate product removal. MTBE is separated from the unreacted hydrocarbons as the bottom pro-

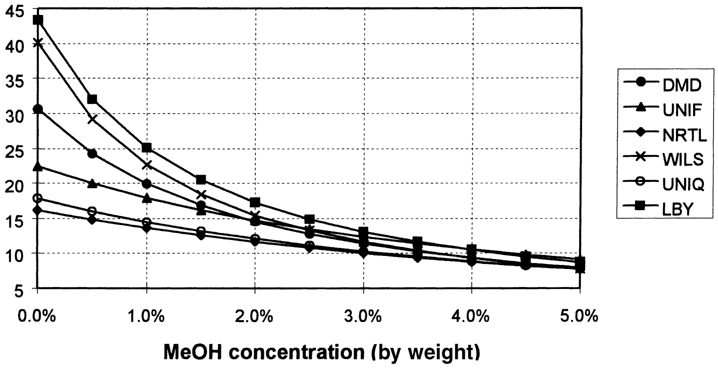

Fig. 1. Activity coefficients for the binary system isobutene/methanol.

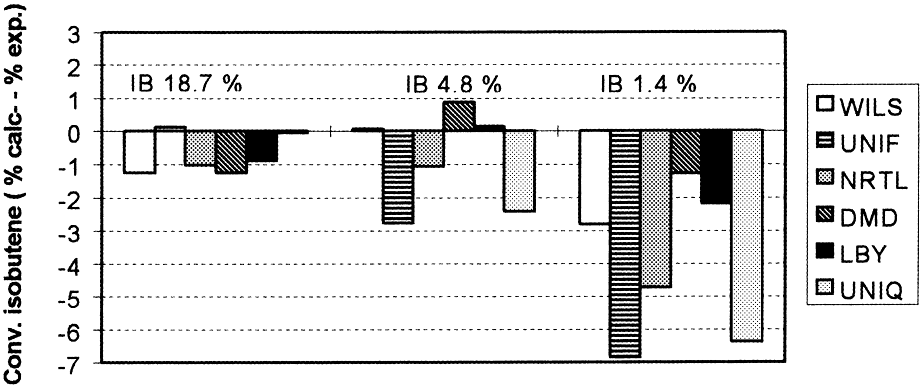

Fig. 2. Equilibrium conversion for different concentrations of isobutene in the C_4 feed (T=50°C, MeOH/isobutene ~1 mol/mol). Predictions of different thermodynamic methods vs. experiments.

duct in two ether fractionators. Unreacted hydrocarbons are treated for methanol removal by water washing. Unreacted methanol is distilled from water and recycled to the synthesis. Heavy by-products as DIB, TBA and MSBE are collected along with MTBE, while DME concentrates in the C_4 raffinate. When the C_4 raffinate is recovered as feedstock for alkylation, DME is removed by a further distillation.

In the Snamprogetti process, the etherification is generally carried out in two reactors; the first one, where most of the isobutene is converted, is a water-cooled multitubular reactor (WCTR). In Fig. 4, typical profiles for the process side temperature (T_{pr}), the cooling water temperature (T_w), the isobutene conversion (CONV) are reported together with the relevant profile for the approach to the thermodynamic equilibrium as expressed by the ratio: $A = K_x K_\gamma / K_{eq,1}$ (i.e. $1-A$ is the driving force for the MTBE formation).

The temperature profile of the WCTR represents the optimal trade-off between kinetics and thermodynamics, i.e. high temperature at reactor inlet, to allow high reaction rates, and low temperature in the outlet zone, to maximize the conversion. Furthermore, it should be observed that in the WCTR most of the isobutene is converted in the first part of the reactor, hence most of the catalyst installed is used as an allowance to cope either with poisoning or with changes in feedstock flowrate and composition.

3. Evolution (MTBE and alkylate co-production)

3.1. Process description

Carrying out the MTBE synthesis under substoichiometric conditions, i.e. MeOH/isobutene

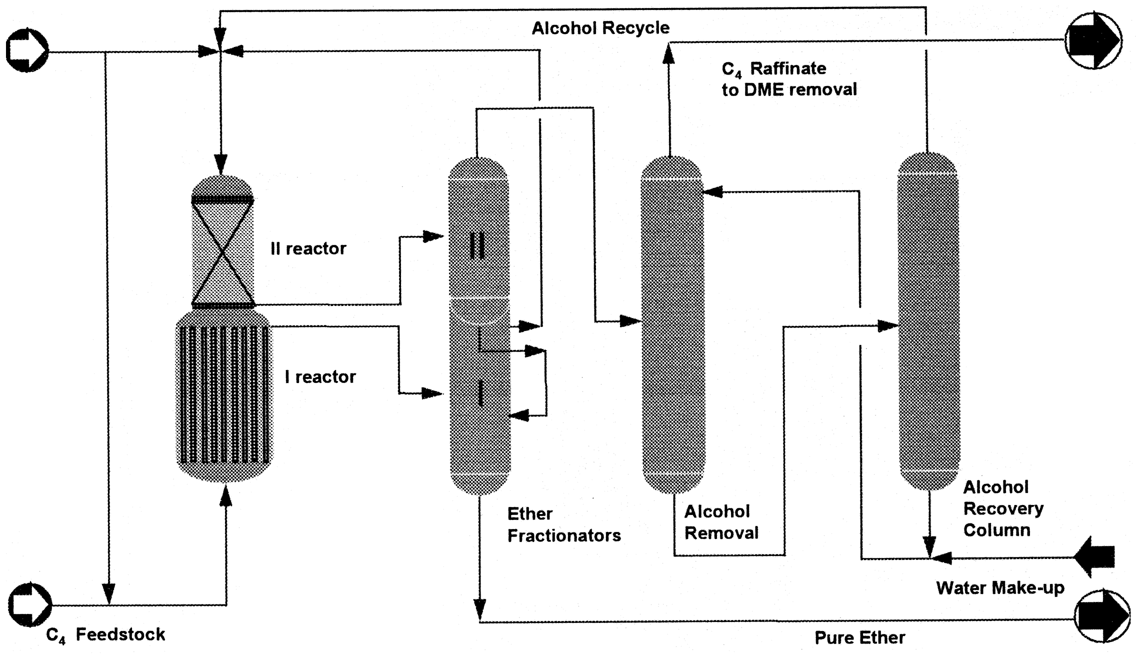

Fig. 3. Snamprogetti high-recovery MTBE plant.

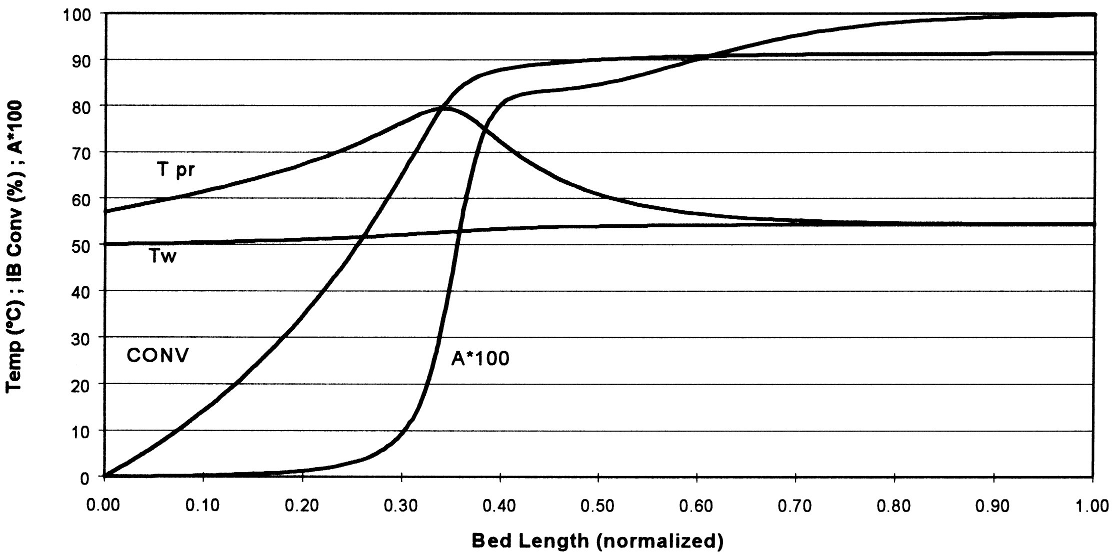

Fig. 4. WCTR. Conversion, temperature and equilibrium approach profiles.

0.2–0.6 mol/mol, it is possible to produce simultaneously and in a wide range of relative ratios MTBE and isobutene dimers (DIB), namely 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene (Fig. 5).

The reaction is selective as trimers may be limited to 5–10% by weight in the hydrocarbon fraction, and only a few thousands of ppms of tetramers are formed.

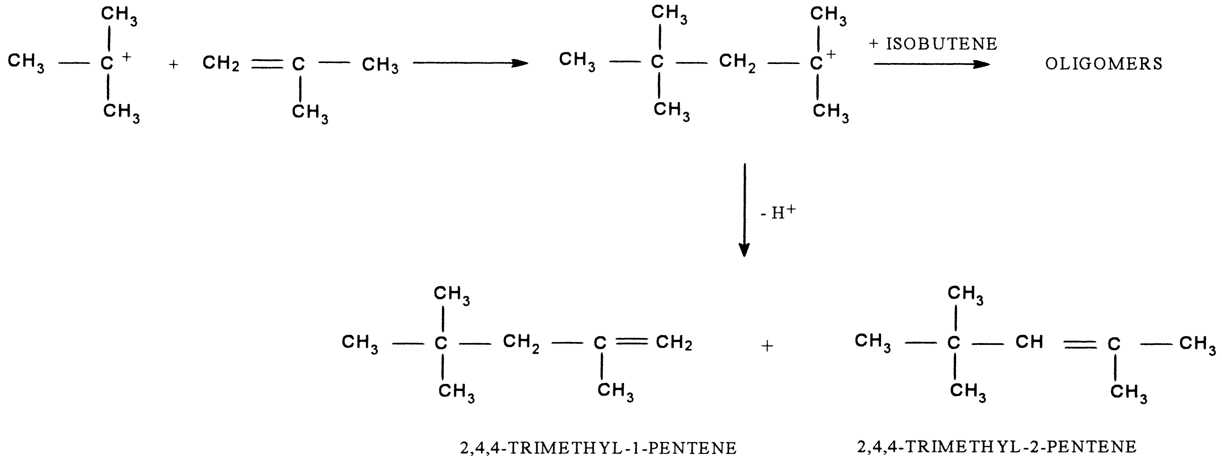

Fig. 5. Isobutene dimerization.

As the hydrogenation of isobutene dimers yields isooctane (2,4,4-trimethyl-pentane), which is both the main component of the alkylate and the reference for rating the gasoline octane properties (RON=100; MON=100), this reaction may be exploited to switch the production of an MTBE plant, according to the market needs, from oxygenate to a high-quality alkylate product, i.e. containing less than 10% by weight of C_{12} species.

A separation column to split MTBE and DIB downstream the ether fractionator and a hydrogenation reactor are the only additional equipments required.

3.2. *Process development*

So far, isobutene dimerization has been scarcely exploited in industrial applications for the production of gasoline components [11]. As a matter of fact this reaction proceeds very quickly even at low temperatures, is exothermic ($\Delta H_r^\circ=-9.5--10.5$ Kcal/mol of isobutene) [12] and is not limited by the thermodynamic equilibrium, therefore its control is difficult and reactor runaway is possible. Indeed, a series of experiments carried out in the absence of methanol using a water-cooled bench scale reactor resulted in great difficulties in maintaining the temperature below 120°C, which is the maximum allowed for stable catalyst operation. A rather low selectivity to dimers, i.e. less than 60%, was obtained. However, these results were in good agreement with previously reported data, despite some difference in experimental set-up and operating conditions (Table 1).

Eventually, this reaction was dropped due to the extensive formation of species which fall in the upper end (C_{12}) or even outside (C_{16}) the gasoline boiling range (35–180°C).

An impressive increase in selectivity to dimers along with a strong decrease in the formation of C_{12}^+ species was instead obtained introducing methanol in the reacting system (methanol/isobutene=0.2–0.6 mol/mol) (Table 2).

As a matter of fact, methanol influences the isobutene dimerization process in a number of ways. First, because of its high polarity, methanol is preferentially adsorbed on the active sites of the catalyst,

Table 1
Isobutene dimerization (product composition)

	(a)	(b)	(c)
Isobutene conversion (%)	86	58	$\leq$99
Product composition (wt%)			
C_8	54	52	58
C_{12}	40	40	38
C_{16}	6	8	4

(a) Isobutene=53% by weight, amberlyst 15, T_{max}=98°C, T_{water}=40°C, LHSV=5.5/h (this work).

(b) Isobutene=30% by weight, Amberlyst 15, T=60°C, LHSV=1/h [13].

(c) Isobutene=45% by weight, acid slurry, $T\cong$100°C [11].

Table 2
Effect of methanol/isobutene molar ratio on selectivity and product composition

	0.2	0.4	0.6
Isobutene (wt%)	46	50	48
Maximum reaction temperature	74	73	72
Cooling water temperature (°C)	40	40	40
Isobutene conversion (%)			
Overall	88	79	79
To MTBE	21	37	60
Product composition (wt%)			
C_8	79.2	88.3	92.6
C_{12}	19.7	10.9	7.1
C_{16}	1.1	0.8	0.3

Catalyst: Amberlyst 15; LHSV=5.5/h.

according to the following reaction:

$$SO_3^-H + MeOH \rightleftarrows MeOH_2^+ + SO_3^-.$$

As $MeOH_2^+$ is a less acid species compared to $SO_3^-H^+$ [14] the rate of the oligomerization reactions is much reduced; this affects positively the selectivity to dimers. Furthermore, since isobutene is more rapidly converted to MTBE than to dimers, the concentration of free isobutene is also reduced, resulting in a lower tendency to oligomerization.

The relative content of linear olefins and paraffins in the feed, which depends on its source (Table 3), is one of the most important factors influencing the selectivity of the reaction.

Through experiments carried out in the bench-scale reactor it was verified that linear butenes positively affect the selectivity to dimers; hence, for the same operating conditions, C_4 feeds from SC and FCC are more selectively converted than feeds from DHY (Table 4).

Since linear butenes are preferentially adsorbed on the catalytic sites with respect to the formed dimers, oligomerization reactions are hindered even when isobutene has been almost completely converted.

Table 3
Typical compositions of C_4 streams from various sources (wt%)

	SC	FCC	DHY
Isobutene	28–46	10–25	45–55
1-Butene	30–45	8–15	0
2-Butenes	5–15	15–35	0
C_4 paraffins	4–8	30–60	45–55

Table 4
Effect of feedstock composition

	FCC	SC	DHY
Isobutene (wt%)	22	38	45
Reaction temperature (max) (°C)	70	75	75
Cooling water temperature (°C)	50	45	40
Isobutene conversion (%)			
Overall	90	89	91
To MTBE	41	42	45
Product composition (wt%)			
C_8	90.3	90.2	88.2
C_{12}	9.4	9.8	11.4
C_{16}	0.3	0.01	0.4
C_8 composition (wt%)			
DIB	69.8	79.4	98.6
DMHE	8.5	14.5	0
TMP	21.7	6.1	1.4

Catalyst: Amberlyst 35; MeOH/isobutene=0.4 mol/mol; LHSV=4.4/h.

On the contrary, as the paraffins cannot be adsorbed on the catalyst, when a feedstock from a DHY unit is used, a slightly higher methanol/isobutene molar ratio must be used in order to minimize the formation of heavy species. Table 4 also shows that the composition of the C_8 fraction is strictly related to the feed type. In fact, when feedstocks from DHY are used, the only possible reaction for isobutene, besides the etherification to MTBE, is the addition to a *tert*-butyl ion to form a higher molecular weight carbocation; this ion eventually adds another molecule of isobutene (oligomerization) or eliminates a proton forming 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene (DIB) (Fig. 5). Instead, when linear butenes are present, i.e. feedstocks from FCC or SC, the mechanism is more complex; in this case, linear butenes may react with isobutene forming codimers. The first step is still the formation of a *tert*-butyl ion, but reactions with isobutene, 2-butenes and 1-butene are now possible; the addition of a linear butene gives a primary carbocation which eventually rearranges forming other trimethyl-pentenes (TMP) (i.e. 2,3,3; 2,3,4; 3,4,4 from 2-butenes) and dimethyl-hexenes (DMHE) (i.e. 2,2 and 2,3 from 1-butene) (Fig. 6). Codimerization reactions are slower than dimerization.

A detailed composition of a typical C_8 product obtained from a SC feed is reported in Table 5.

Also the octane quality of the hydrogenated dimers mixture may depend on the feedstock composition.

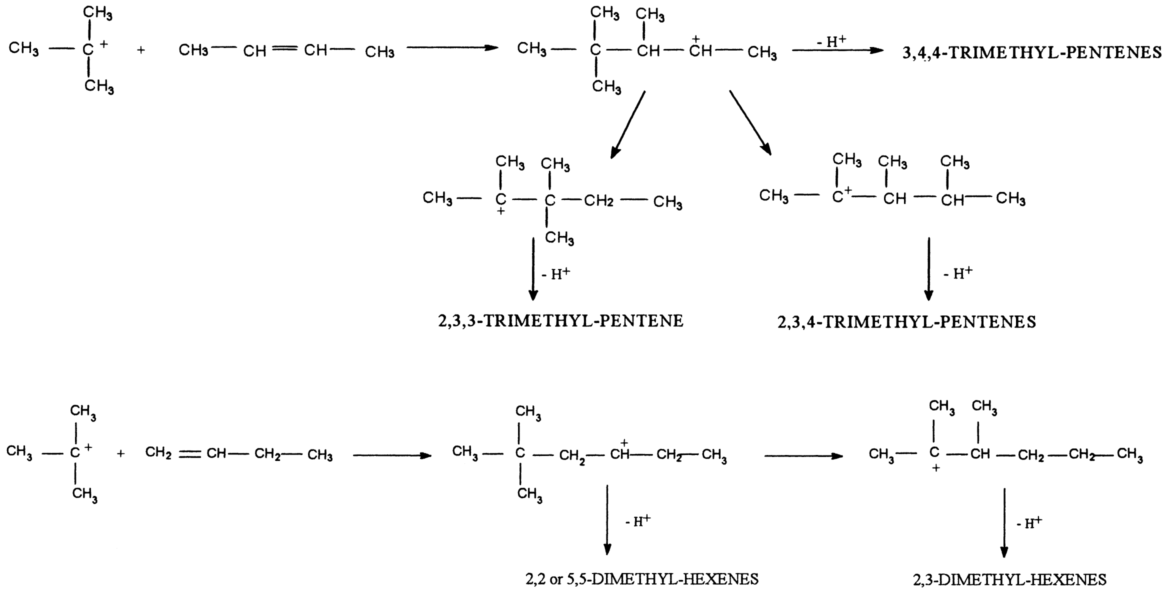

Fig. 6. Isobutene codimerizations with *n*-butenes.

For instance, the product obtained from a SC feed has the lowest octane rating because of the higher content of dimethylhexanes formed from 1-butene. C_4 cuts from DHY units yield the best product having properties similar to pure isooctane (RON=MON=100) as codimerization reactions cannot occur. Both FCC feeds and hydro-isomerized C_4 cuts from SC give products rich in trimethyl-pentanes other than isooctane having intermediate octane properties.

The characteristics of two products containing more than 90% by weight of dimers are reported in Table 6 for a comparison with typical HF and H_2SO_4 alkylates.

As it can be seen, the etherification/dimerization product has better properties compared to alkylate: particularly the octane number is higher and the volatility is lower; furthermore, it is produced in an environmentally-friendly way.

Table 5
Composition of a C_8 olefinic fraction from a steam-cracking feed

Species	ID	Wt%
2,4,4-Trimethyl-1-pentene	DIB	61.98
2,4,4-Trimethyl-2-pentene	DIB	17.40
2,2-Dimethyl-hexenes	DMHE	7.55
2,3-Dimethyl-hexenes	DMHE	6.62
2,3,3-Trimethyl-pentenes	TMP	0.72
2,3,4-Trimethyl-pentenes	TMP	1.63
3,4,4-Trimethyl-pentenes	TMP	3.80
Other dimethyl-hexenes	DMHE	0.30

3.3. *Pilot plant tests*

To verify the laboratory results and to evaluate the performance of different reactor configurations, an extensive experimentation was carried out on a pilot-plant (Ravenna, Italy) whose scheme is presented in Fig. 7.

Methanol and C_4 hydrocarbons are taken as side streams of a MTBE plant owned by Ecofuel. The reactor is a tube homologous to those used in Snamprogetti WCTRs. Reaction is monitored by 12 thermocouples (RT01-RT12) distributed along the reactor length in correspondence of 12 sampling valves. Heat of reaction may be removed by circulating water in an external jacket while draining the jacket the reactor may be operated adiabatically. The reactor adiabaticity was assessed by checking the energy balance, i.e. by comparing the observed reactor outlet temperature with values calculated through the knowledge of the effluent composition and reaction enthalpies; the observed temperature increases were only 5–10% lower than the calculated ones.

The influence of the methanol/isobutene molar ratio, *R*, on product composition was studied by

Table 6
Comparison between properties of etherification/dimerization products and typical alkylates

	DHY	SC	HF alkylate	HF alkylate
Clear octane numbers				
RON	100	100	96	97
MON	100	97	94	94
Specific gravity (g/cm^3)	0.72		0.70	
RVP (kPa)	12		31	
ASTM distillation (vol%) (°C)				
IBP	93		40	
10	97		76	
30	98		100	
50	99		104	
70	101		107	
90	113		125	
95	170		171	
EBP	201		196	

processing a C_4 feedstock from SC after butadiene extraction; the isobutene content varied from 28% to 50% by weight. The reactor was first operated at R=1 (i.e. typical MTBE synthesis condition), afterwards the methanol feed was progressively reduced up to R=0.2. A reduction in the selectivity to dimers was observed. However, at R=0.3 they still accounted for about 90% of the whole hydrocarbon fraction (Fig. 8).

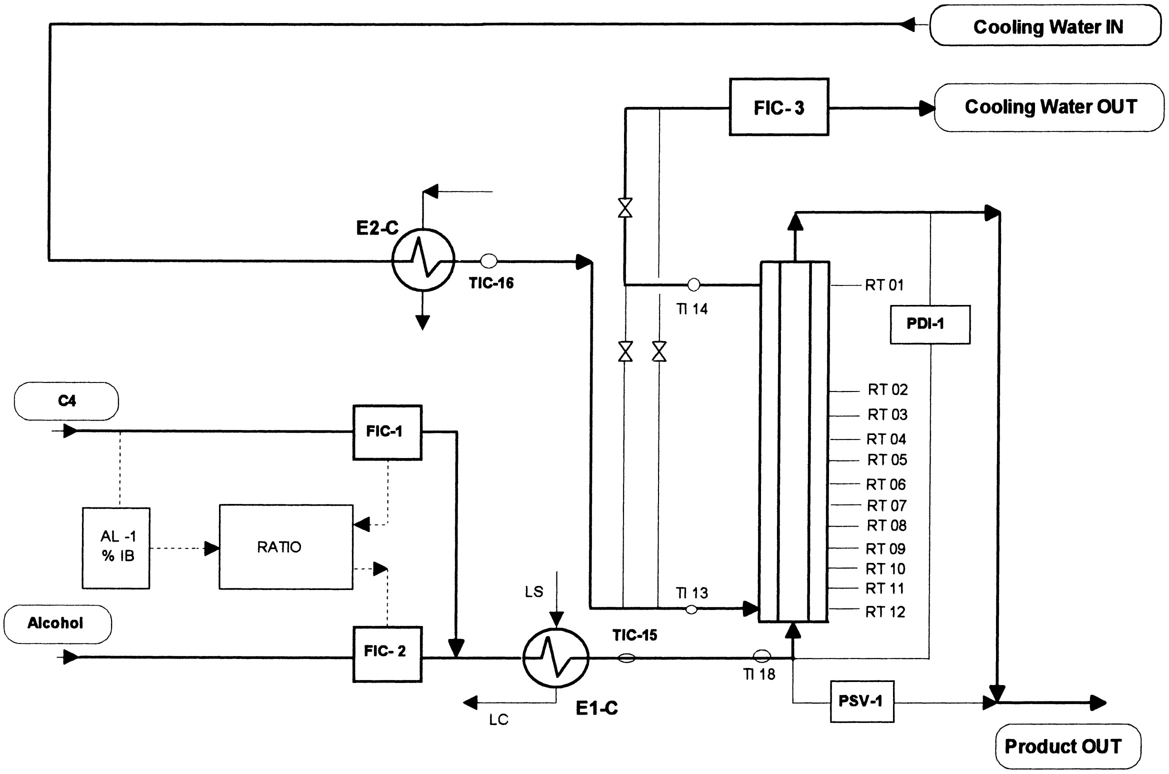

Fig. 7. Pilot plant scheme.

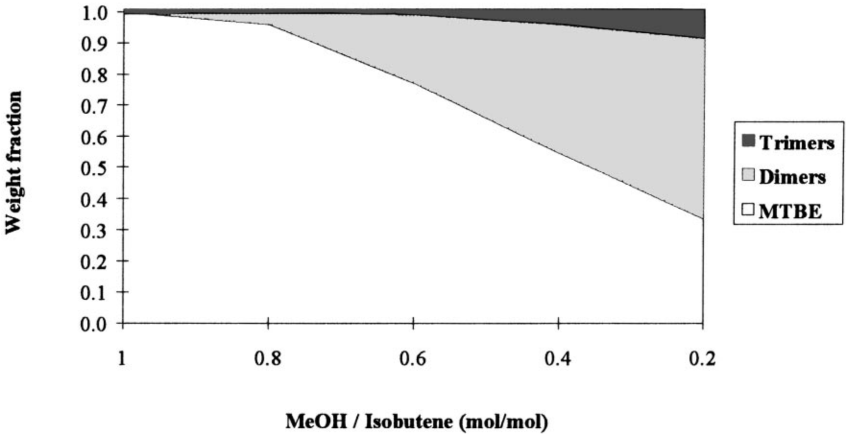

Fig. 8. Etherification/dimerization of isobutene. Typical product composition.

In Fig. 9 profiles obtained during pilot plant runs under typical MTBE (R=1) and dimerization conditions (R=0.3) are compared. The reactor was operated with heat removal. It can be seen that in the latter case the temperature profile was much sharper, and in the first part of the reactor, more isobutene was converted both to MTBE and to dimers.

Although much less methanol was used with respect to the MTBE synthesis, isobutene was selectively converted to MTBE in the first part of the reactor. Only when methanol was almost completely converted, i.e. the MTBE equilibrium was approached, dimerization became the main reaction. It is worth noting that under dimerization conditions the isobutene conversion increased along the whole catalytic bed, while in the MTBE synthesis a steady level corresponding to the thermodynamic equilibrium was approached. This means that, per pass, more isobutene can be converted to dimers than to MTBE since isobutene dimerization is not an equilibrium limited reaction.

Further, to assess the influence of different reactor configurations on the synthesis, runs under adiabatic conditions were performed. In Fig. 10 typical temperature and composition profiles are reported. A steady temperature between 100° and 110°C was always approached at reactor outlet.

Actually, as the reactor runaway was considered likely to occur in these tests, this behaviour was rather unexpected. In fact, through the presence of methanol, an otherwise impossible smooth control of the adiabatic dimerization process was achieved, although most of the reactor worked close to the threshold for the catalyst stability.

The steady temperature reached in the adiabatic runs proves that the heat released by the isobutene dimerization ($\Delta H_r = -9.5 - -10.5$ Kcal/mol of isobutene) [12] may be completely taken up by the endothermic MTBE decomposition reaction ($\Delta H_r = +9.5$ Kcal/mol); indeed, for temperatures higher than 100°C these two reactions proceed at similar rates, as it can be seen by composition profiles in Fig. 10.

It should be noted that more dimers were produced in the adiabatic runs because the higher the temperature the lower the MTBE equilibrium concentration, but also the undesired methyl-*sec*-butyl ether (MSBE) which has poor octane properties (RON, MON<80) was more extensively formed (5% vs. 0.1–0.3% by weight).

However, even when MSBE cannot be formed, as when a feedstock from a DHY unit is processed, the reaction is preferentially carried out providing heat transfer, since a too fast catalyst aging may occur due to the higher temperatures of the adiabatic operation.

Finally a life test was carried out for over 2500 h at R=0.3. These conditions were corresponding to an overall flow of more than 40 m^3 of C_4 hydrocarbons per kg of resin. As it was known that a build-up of oligomers in the macroporous structure of the resin hinders the access of the reactants to the acidic sites and swells the particles, both a decay in isobutene conversion and an increase of the pressure drops through the reactor were expected.

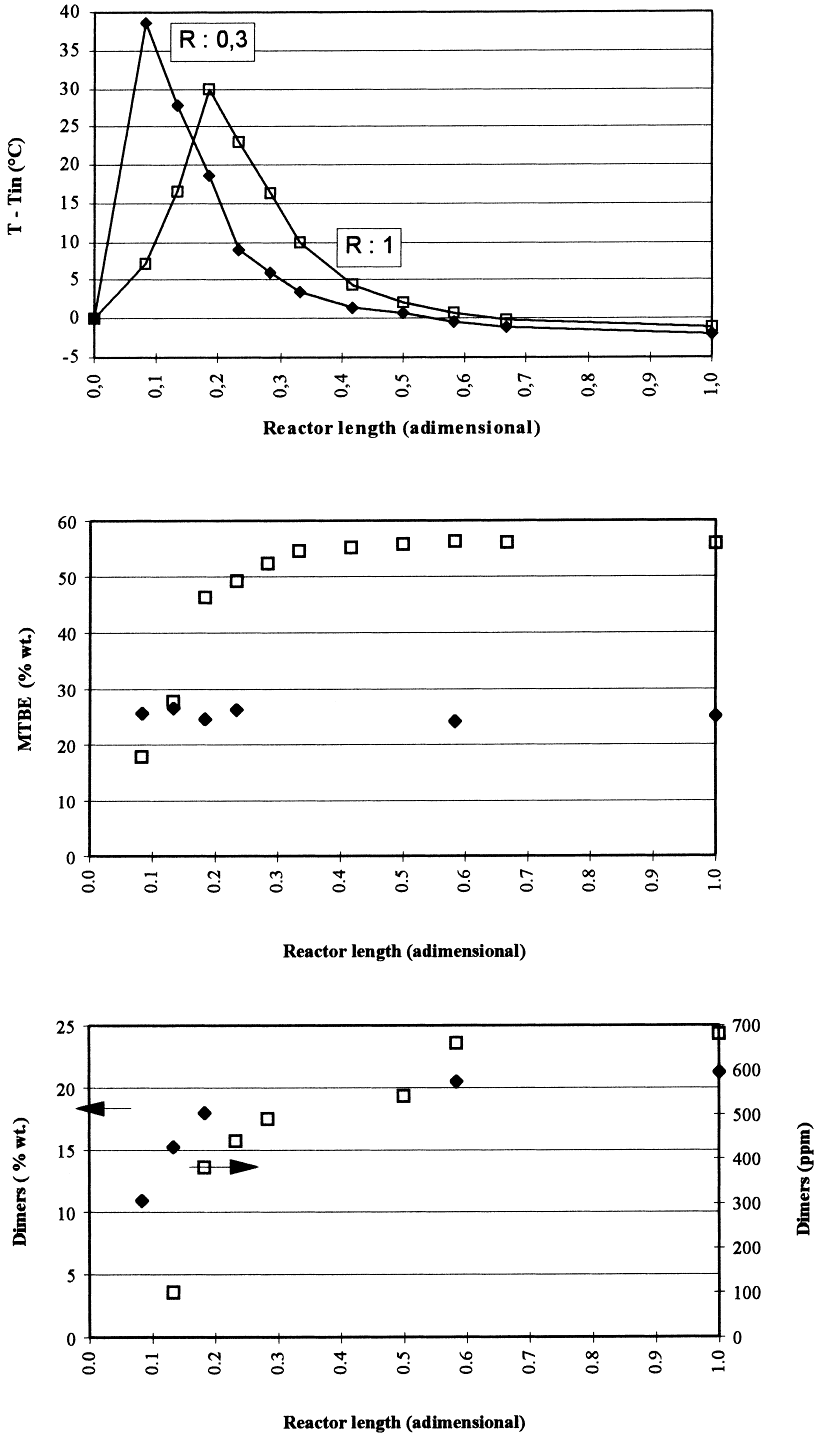

Fig. 9. Temperature and products profiles. *R*: ◆, 0.3; □, 1. T_{in} (reactor inlet temperature)=58°C, LHSV=7/h, isobutene=45 wt%, catalyst: Amberlyst 35.

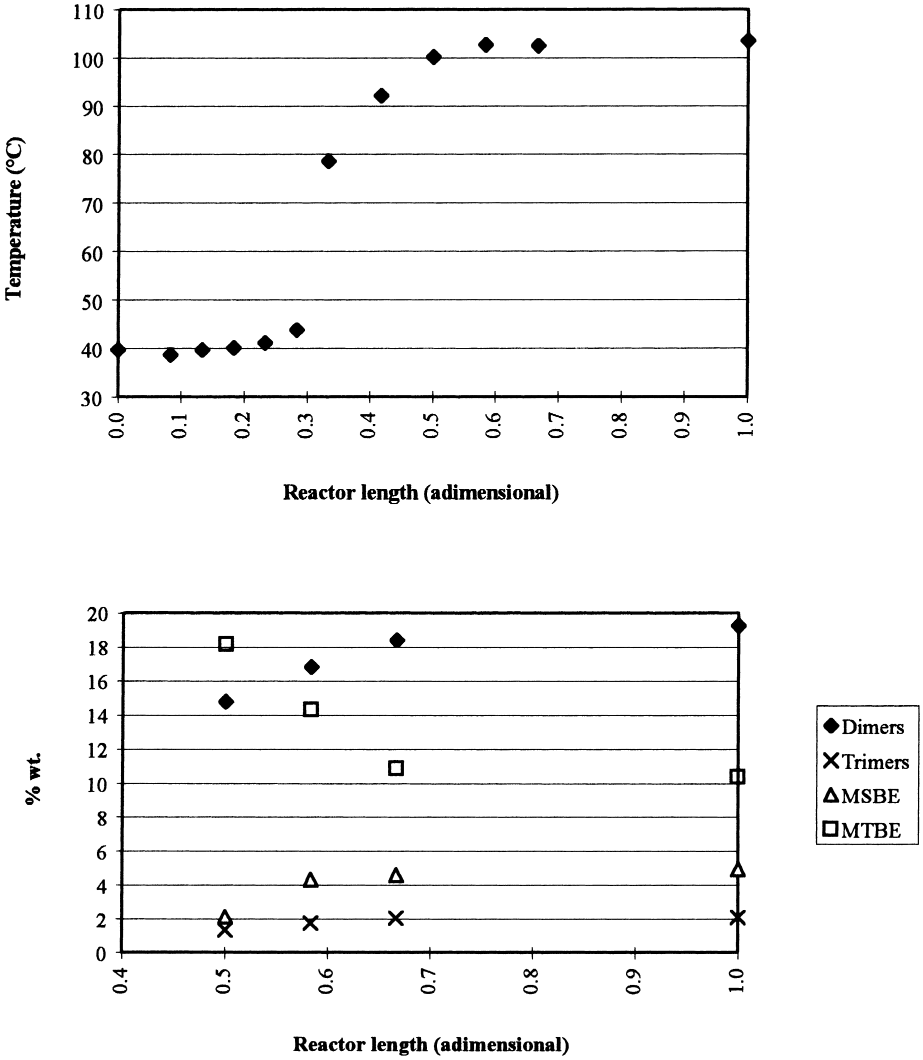

Fig. 10. Adiabatic runs. Temperature and products profiles. R=0.4, LHSV=7/h, isobutene=28 wt%.

Surprisingly, steady isobutene conversion and C_8 selectivity were observed. Pressure drops even lower than in the MTBE synthesis were recorded as the catalyst shrinkage due to the reduced concentration of methanol inside the reactor offset any other effect. Actually, analyses performed over unloaded catalyst samples revealed that the actual deactivation mechanisms were similar to those occurring in the MTBE synthesis, i.e. adsorption of metal cations and basic compounds rather than pore plugging; therefore it was concluded that the simultaneous etherification/dimerization might be carried out without problems in commercial MTBE plants.

3.4. Operating experience

According to these positive results, the very first industrial combined production of MTBE and isobutene dimers was carried out on March 1997 in one of the Ecofuel's MTBE plants (Ravenna, Italy) whose scheme is similar to the one reported in Fig. 3.

The test was limited to producing the MTBE/dimers mixture in the WCTR.

The most relevant results of this operating experience were the following:

- the overall isobutene conversions exceeded 99%;
- the residual isobutene in the C_4 raffinate complied with the commercial specifications (<0.3% by weight) for its use as a feedstock for 1-butene extraction plants;
- more than 800 tons MTBE/dimers mixture were produced: the average hydrocarbon content was about 35% by weight; the concentration of C_{12} in the hydrocarbon fraction was lower than 8% by weight. Only 2000 ppm of C_{16} were detected as the heaviest by-products.

The MTBE/dimers mixture was commercialized without further treatments; its octane number was very similar to MTBE.

4. Conclusions

The MTBE process may be modified in order to produce, in an environmentally-friendly way, a mixture of oxygenate and high-octane branched hydrocarbons (mainly isooctane) having characteristics similar or even better than alkylate made by conventional technologies using HF or H_2SO_4.

This new technology has been already tested on the industrial scale in the Ecofuel's MTBE plant in Ravenna, Italy.

We believe it may represent an attractive option for industrial applications as it brings flexibility both to already existing and future MTBE plants. These could be run in the most effective way in order to fulfil the market needs for oxygenates and alkylate; as a matter of fact, MTBE and hydrocarbons could be obtained in the desired proportions just varying the amount of methanol fed to the plant.

A separation column and a hydrogenation section are the only additional items required to transform a MTBE plant into a complex for the co-production of MTBE and alkylate.

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References

[1] G.H. Unzelman, Proceedings of the NPRA Annual Meeting, San Antonio, Paper AM-97-26, 1997.
[2] P. Rao, S.R. Vatcha, Oil Gas J. 9 (1996) 56.
[3] I. Miracca, L. Tagliabue, R. Trotta, Chem. Eng. Sci. 51 (1996) 10, 2349.
[4] J. Gmehling, J. Li, M. Schiller, Ind. Eng. Chem. Res. 32 (1993) 178.
[5] B.L. Larsen, P. Rasmussen, A. Fredenslund, Ind. Eng. Chem. Res. 26 (1987) 2274.
[6] G.M. Wilson, J. Am. Chem. Soc. 86 (1964) 127.
[7] H.K. Hansen, P. Rasmussen, A. Fredenslund, M. Schiller, J. Gmehling, Ind. Eng. Chem. Res. 30 (1991) 2352.
[8] D.S. Abrams, J.M. Prausnitz, AIChE J. 21 (1975) 116.
[9] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135.
[10] L. Tagliabue, M. Di Girolamo, E. Pescarollo, Proceedings of the Second Italian Conference on Chemical Engineering, Florence, 1995, p. 138.
[11] G. Scharfe, Hydrcarbon Process 53 (1973) 4, 171.
[12] A. Rehfinger, U. Hoffmann, Chem. Eng. Technol. 13 (1990) 150.
[13] W.O. Haag, Chem. Eng. Prog. Symp. Ser. 63 (1967) 140.
[14] B.C. Gates, W. Rodriguez, J. Catal. 31 (1973) 27.