

# Separation of alcohol/ether/hydrocarbon mixtures in industrial etherification processes for gasoline production

C. Streicher\*, L. Asselineau\*, A. Forestière\*\*

\* Institut Français du Pétrole, 1 et 4 avenue de Bois Préau, BP 311, 92506 Rueil-Malmaison Cedex, France

\*\* CEDI - BP 3, 69390 Vernaison, France

## Abstract

Ether synthesis is growing in importance in the oil industry, due to their increasing use as octane enhancers in gasolines.

Ethers are obtained by the addition of an alcohol on an iso-olefin. The main ethers of industrial interest for gasolines are:

- MTBE (methyl tert-butyl ether) resulting from the addition of methanol on isobutene.
- TAME (tert-amyl methyl ether) resulting from the addition of methanol on isoamylenes.
- ETBE (ethyl tert-butyl ether) resulting from the addition of ethanol on isobutene.

The reaction step of etherification processes yield rather complex mixtures of alcohols, ethers and hydrocarbons which are difficult to separate due to the existence of numerous azeotropes. After reviewing the use of ethers as gasoline components this paper describes the separation steps which are involved, in the case of ETBE synthesis. It is particularly shown that an accurate knowledge of the thermodynamical behaviour of ethanol/ETBE/C<sub>4</sub> mixtures is essential for the design of these separation steps.

## 1. INTRODUCTION

Increasing environmental concern and the subsequent emergence of more stringent regulations on fuel engines exhaust gases are leading to progressive changes in gasoline composition. Among these changes the ban on lead additives, mainly because of their poisonous effects on exhaust catalytic mufflers, is probably the most significant. This led refiners to increase gasoline contents of other hydrocarbon components having high octane numbers, like branched paraffins and aromatics, or to look for new octane enhancers. But, due to the toxicity of aromatic compounds, their levels will rather be reduced than increased thus limiting the available options.

Oxygenated compounds like alcohols or ethers have high octane numbers, as can be seen from table 1. Furthermore the incorporation of oxygenated compounds in gasoline reduces the emissions of CO and of unburned hydrocarbons in engines exhaust gases. But ethers have specific advantages over alcohols which make them more suitable as octane enhancers for gasolines. Among these advantages are the facts that:

- ethers, unlike alcohols, don't demix in the presence of water thus reducing the contamination of the water which is generally found in the bottom of most gasoline storage tanks,
- their vapor pressure in mixture with hydrocarbons is lower than that of alcohols (see table 1).

This is why etherification processes are now being developed very rapidly in the refining industry (see § 2).

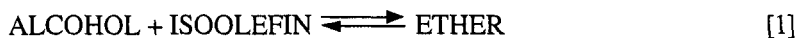
TABLE 1. Selected properties of some ethers and alcohols compared with those of premium gasoline

Property	Premium	MTBE	ETBE	TAME	Methanol	Ethanol	TBA
Density (kg.m <sup>-3</sup> )	735-760	746	750	750	796	794	792
Boiling point (°C)	30-190	55.3	72.8	86.3	64.7	78.3	82.2
Vapor pressure blending (bar)	0.7-0.8	0.55	0.4	0.1	5.24	1.54	1.03
Heat of combustion (KJ/l)	32020	26260	26910	27375	15870	21285	25790
Heat of vaporization (KJ/l)	289	337	321	310	1100	854	510
Octane number ((R + M) / 2)	90	110	112	107	112	110	100

## 2. ETHER SYNTHESIS FOR GASOLINE PRODUCTION

### 2.1. Reactions and yielded products

The ethers used as gasoline components are obtained by the addition of an alcohol on an isoolefin, according to the following general reaction scheme:



Although there is in principle no limitation in the number of carbon atoms of either the alcohol or the isoolefin, the thermodynamical equilibrium of reaction [1] becomes less favourable to the formation of the ether when the number of carbon atoms of the reagents increases. This is one of the reasons why at present the most widely used ether in gasoline is MTBE (methyl tert-butyl ether) obtained from methanol and isobutene according to the following reaction:



One other reason being the fact that the etherification of isobutene provides a good way to put more C<sub>4</sub> in gasoline without increasing its vapor pressure.

But as can be seen from table 2 the synthesis of many other ethers from either higher alcohols (ethanol, isopropanol, ...) or from higher isoolefins (C<sub>5</sub>, C<sub>6</sub>...) has already been considered (1, 2).

TABLE 2. Potential ethers for gasolines, from (1, 2)

	Hydrocarbon	Alcohol	Ether
C <sub>4</sub>	Isobutene	Methanol	Methyl tert-butyl ether (MTBE)
	Isobutene	Ethanol	Ethyl tert-butyl ether (ETBE)
	Isobutene	Isopropyl alcohol	Isopropyl tert-butyl ether (IPTBE)
C <sub>5</sub>	2 methyl 2 butene } 2 methyl 1 butene }	Methanol	Tert-amyl methyl ether (TAME)
	2 methyl 2 butene } 2 methyl 1 butene }	Ethanol	Ethyl tert-amyl ether (ETAE)
C <sub>6</sub>	2 methyl 1 pentene } 2 methyl 2 pentene }	Methanol	2 methyl 2 methoxy pentane
	3 methyl 2 pentene } 2 ethyl 1 butene }	Methanol	3 methyl 3 methoxy pentane
	2,3dimethyl 1 butene } 2,3 dimethyl 2 butene }	Methanol	2,3 dimethyl 2 methoxy butane
	1 methyl cyclopentene	Methanol	1 methyl 1 methoxy cyclopentane
	C <sub>7</sub>	22 different isoolefins	Methanol
	-	Isopropylalcohol	Diisopropylether (DIPE)*

\* not formed according to the general reaction scheme [1]

## 2.2. Ethers market

The very rapid increase of the MTBE production capacity is illustrated in Fig. 1.

This fast growth is expected to go on for the following next years, as recent regulations like the "Clean Air Act" in the USA will increase oxygen levels in gasolines up to 2 wt %, corresponding to 9 wt % of MTBE, or even more. Therefore the world MTBE production capacity should reach 30 billions of tons per year at year 2000 or even before.

Due to this high increase in MTBE demand, isobutene availability in refineries may become a limitation for etherification processes.

This is why the etherification of higher hydrocarbons (C<sub>5</sub>, C<sub>6</sub> mainly) is also expected to develop. The etherification of an olefinic C<sub>5</sub> or C<sub>6</sub> cut has as further advantage to reduce its olefinic content which is also environmentally favourable, light olefins being suspected to take part in tropospheric ozone formation.

The use of ethanol instead of methanol for etherification purposes was until now hindered because of the much higher cost of ethanol. As tax incentive policies are being developed or likely to be developed in several western countries for the fuel uses of agricultural ethanol, ETBE synthesis plants are likely to be built or some existing MTBE plants might be converted to ETBE production.

MTBE production capacity in 10<sup>6</sup> t/years

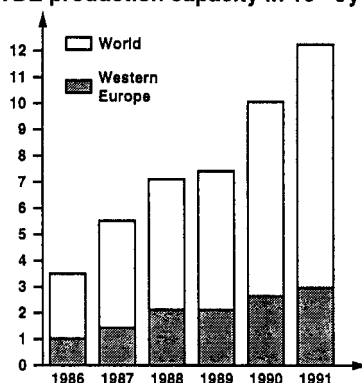


Fig. 1. MTBE production capacity, in 10<sup>6</sup> t/year

## 2.3. Etherification processes

The etherification reaction is done in liquid phase, at moderate temperature (below 100°C) on a catalyst which is an acidic ion exchange resin, in one reactor or in two reactors in series. The isoolefins used as reagents are generally used in mixture with other hydrocarbons of similar boiling points. For instance isobutene feedstocks for MTBE usually are C<sub>4</sub> cuts from Fluid Catalyst Cracking plants, from Steam Cracking plants or from field butanes Dehydrogenation/Isomerization plants. Depending on their origin, these C<sub>4</sub> cuts usually contain between 20 and 50 wt % isobutene. The etherification reaction is highly selective so that nearly only the isoolefins are converted to ethers.

An excess of alcohol is usually fed to the reactor(s) in order to achieve high conversions of the isoolefins.

The effluent of the reaction steps is then a mixture of the ether produced with the unreacted or non reactive alcohol and hydrocarbons, with some other minor impurities coming from side reactions. These side reactions will be illustrated in § 3.1 in the particular case of ETBE synthesis.

This mixture generally has to be separated into:

- an ether fraction to be blended with gasoline,
- an hydrocarbon fraction to be further processed in refining operations (alkylation, isomerization, ...),
- an alcohol fraction to be recycled to the etherification reactor(s).

The first step of the split-up of this mixture is an azeotropic distillation producing the ether as bottom product and the hydrocarbons as top product. The alcohol splits up between the top and the bottom so that further alcohol/hydrocarbons and/or alcohol/ether separations have to be performed. The split-up of the alcohol between top and bottom products depends on the nature of the compounds which are used. For instance in MTBE processes all the methanol is generally recovered with the C<sub>4</sub> hydrocarbons and pure MTBE is produced at the bottom. This will be now illustrated in more details in the particular case of ETBE synthesis.

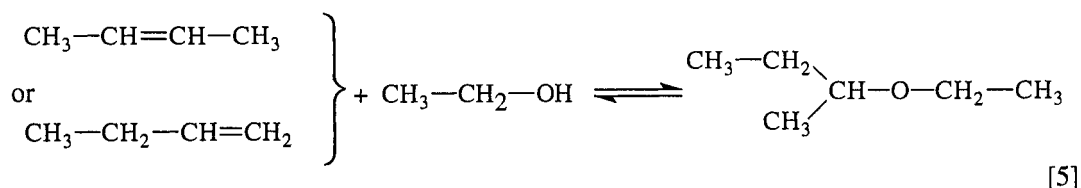
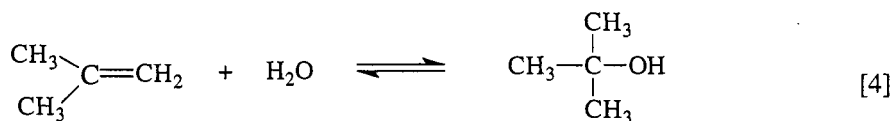
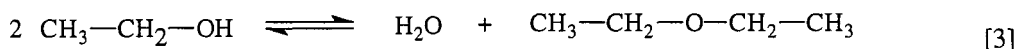
It must be pointed out that in some processes this azeotropic distillation is modified into a catalytic distillation where catalyst is put on some of the trays of the distillation column. This allows the etherification reaction to further progress as the ether produced is removed from the hydrocarbons. In this case higher conversion rates of the isoolefins can be achieved and/or lower excess of alcohol can be used which may simplify the further separation steps.

### 3. SEPARATION OF ETHANOL/ETBE/C<sub>4</sub> MIXTURES

#### 3.1. ETBE synthesis

IFP has now a several years experience of industrial ETBE synthesis, on a plant located at ELF refinery FEYZIN, near LYON (FRANCE) (3,4).

In addition to ETBE, unreacted C<sub>4</sub> hydrocarbons and ethanol the effluent of the reaction steps also contains minor parts (usually less than 1 wt % for each component) of other oxygenated compounds: water, DEE (diethyl ether), TBA (tert-butyl alcohol) and ESBE (ethyl sec-butyl ether) which are products from the following side reactions



#### 3.2. Separation processes in ETBE synthesis

As was already mentioned in § 2.3 the separation of the ethanol/ETBE/C<sub>4</sub> mixtures starts with an azeotropic distillation also called debutanizer (in some cases it can be a catalytic distillation) which produces as top product a C<sub>4</sub>/ethanol mixture and as bottom product an ETBE/ethanol mixture.

The oxygenated impurities split-up as follows:

- all the water is recovered with the C<sub>4</sub> hydrocarbons
- nearly all the other oxygenated compounds (TBA, DEE, ESBE) are recovered with the ETBE.

In addition the ETBE bottom product also contains some part of heavier hydrocarbons (C<sub>5</sub><sup>+</sup>) either present in the reactor C<sub>4</sub> feedstream or formed during the reaction step by butenes oligomerization.

Ethanol is then removed from the C<sub>4</sub> hydrocarbons by water washing and ethanol/water distillation according to the scheme of Fig. 2. The distillation of the ethanol/water mixture produced by the water washing yields an azeotropic ethanol/water mixture which, although containing relatively high amounts of water, can be recycled to the reactor(s). In fact the amount of water thus fed to the reactor(s) represents only roughly 50% of the total water fed to the reactor(s). This water then gives rise to the formation of TBA according to reaction [4].

The water washed C<sub>4</sub> hydrocarbons can then be further processed, if necessary after some final purification (e.g. by adsorption of residual oxygenated compounds).

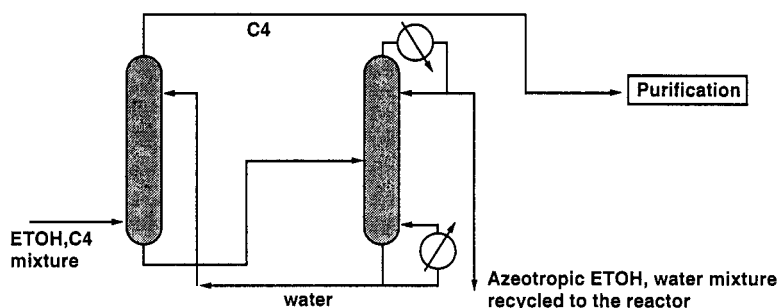


Fig. 2. Ethanol/C<sub>4</sub> separation process

Ethanol and ETBE form azeotropes (e.g. at 22.4 wt % ethanol under atmospheric pressure) so that they cannot be separated by simple distillation. Several rather complex separation schemes were therefore proposed for this mixture (5), (6), (7). But at present the simplest separation scheme is a two distillation process (7), shown in Fig. 3, which is based on the change of ethanol/ETBE azeotropic composition with pressure.

This process produces ETBE, with only the heaviest impurities like ESBE or butenes oligomers, at the bottom of the high pressure distillation, and an ethanol/TBA mixture which can be recycled to the reactor(s) at the bottom of the low pressure (usually atmospheric) distillation.

In order to avoid build-up of lighter impurities, like DEE or C<sub>5</sub> hydrocarbons, a purge has to be done from the recycled mixtures recovered at the heads of these distillations.

### 3.3. Design of the debutanizer

As can be seen from the above description of the separation processes involved in ETBE synthesis the design of the debutanizer, which is the initial separation step, is critical because it defines the split-up of ethanol and the other oxygenated impurities between the C<sub>4</sub> hydrocarbons and the ETBE streams, which in turn is the basis for the design of further separation steps.

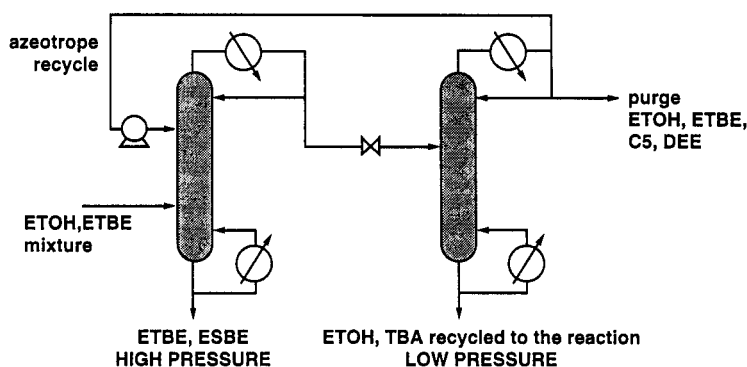


Fig. 3. Ethanol/ETBE separation process

In addition an accurate simulation of the ethanol profile of the column is also essential for the design of catalytic distillation.

In order to study the ethanol split-up at different amounts of ethanol in the Ethanol/ETBE/C<sub>4</sub> mixture to be separated, the composition of the reactor(s)' effluent mixture was calculated for different stoichiometric ratios of ethanol over isobutene and this for a given C<sub>4</sub> feedstream, the composition of which is given in table 3. Each effluent composition then corresponds to a certain conversion rate.

In each case the distillation of the corresponding mixture was then simulated with the column parameters indicated in table 4.

TABLE 3. C<sub>4</sub> feedstream composition in wt %

C3	1,50
n-butane	7,51
isobutane	26,04
isobutene	20,92
butene 1	12,00
butene 2 T	18,01
butene 2 C	13,01
butadiene 1-3	0,01
C <sub>5</sub> <sup>+</sup>	1,00

TABLE 4. Debutanizer parameters

theoretical trays	34
feed tray number*	20
pressure (top)	8.55 bar
reflux ratio (mol)	0.8

\* trays are numbered from 1(top) to 34 (bottom)

The thermodynamical model used to perform the debutanizer simulation is NRTL with activity coefficients for L-V equilibria determined experimentally for ethanol/C<sub>4</sub> (see § 3-4 hereafter) and ethanol/ETBE, and predicted by UNIFAC (bank SIMSCI) in the other cases.

The results of these simulations are shown in Fig. 4 as curves giving the ethanol content in the hydrocarbons top product and in the ETBE bottom product as a function of the isobutene conversion rate.

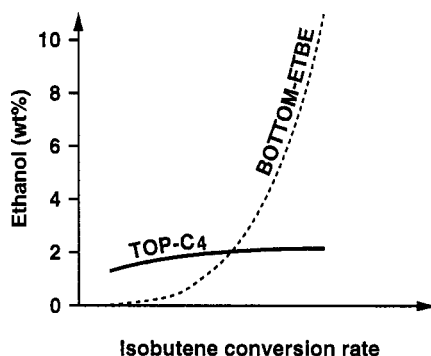


Fig. 4. Ethanol content in the debutanizer top and bottom products vs isobutene conversion rate

It appears clearly from these curves that when the conversion rate increases, i.e. when the amount of ethanol increases, ethanol is first taken out with the top hydrocarbons product up to a certain limit, probably where the ethanol/C<sub>4</sub> azeotropic composition is reached. At higher ethanol amounts the ethanol/C<sub>4</sub> composition remains fairly constant, the ethanol in excess being recovered with the ETBE bottom product.

It also appears that the production of pure ETBE (e.g. with less than 1 wt % residual ethanol) is incompatible with the achievement of high isobutene conversion rates (e.g. more than 90 %).

#### 3.4. C<sub>4</sub>/Ethanol azeotropes

From the above study an accurate knowledge of the azeotropic composition of ethanol/C<sub>4</sub> hydrocarbons mixtures, under process conditions (i.e. moderately high pressures, between 5 and 15 bar), appears essential for process design.

The composition of azeotropic mixtures between ethanol and different pure C<sub>4</sub> hydrocarbons was therefore determined, under a pressure of 8.28 bar, with the following method.

Liquid-vapour equilibria are calculated at bubble point under the given pressure and the ethanol content of the liquid is changed iteratively until the vapour ethanol content equals that of the liquid.

The thermodynamical model chosen for these calculations is NRTL, with two different sets of activity coefficients:

- predicted by UNIFAC (bank SIMSCI)
- determined experimentally.

In the latter case actual liquid-vapour equilibria were determined only with butene 1/ethanol and with n-butane/ethanol mixtures. The activity coefficients thus derived were then used respectively to simulate the behaviour of other butenes/ethanol and isobutane/ethanol mixtures.

Liquid-vapour equilibria experiments were performed at IFP with the apparatus and method described by FRÅNSSON & al. (8) at 50°C and at 100°C, which covers the actual conditions of the industrial process (the temperature at the top of an ETBE debutanizer is around 60-70°C).

The results of these azeotropic compositions determinations are shown in table 5.

TABLE 5. Ethanol content in wt % of the azeotropes with C<sub>4</sub> hydrocarbons under 8.28 bar

	Experimentally determined activity coefficients	UNIFAC predicted activity coefficients
n-butane	1.55	none
isobutane	none	none
isobutene	1.91	none
butene 1	2.12	none
butene 2T	3.54	0.72
butene 2C	4.04	1.79

It is clear than in these cases UNIFAC predicted activity coefficients underestimate the azeotropic ethanol content by roughly 2 wt %, thus making experimental liquid-vapour equilibria determinations necessary.

#### 4. CONCLUSION

The rapid growth of the demand for ethers as gasoline components, mainly for environmental safety reasons, leads not only to the development of the world MTBE production capacity but also to the emergence of other new etherification processes.

Separation steps in these processes can account for more than 50 % of total capital costs and 90 % of total energy consumptions. The separation of Ethanol/ETBE/C<sub>4</sub> hydrocarbons mixtures for instance, requires the installation of 4 distillation columns and one water washing column.

The design of these separation steps is based on the knowledge of the thermodynamical behaviour of rather complex alcohols/ethers/hydrocarbons mixtures, for which predictive methods like UNIFAC may become inaccurate. Thus experimental measurements are needed especially in the actual process temperature and pressure ranges (50-200°C, 5-20 bar).

At last, as most of the difficulties encountered in the separation of these mixtures comes from the many azeotropes which are formed between alcohols, ethers and hydrocarbons, new cheaper processes, able to separate these azeotropes would be needed in order to achieve better separation processes. This is a field were techniques like pervaporation could be used with benefit, most likely in combination with existing distillations.

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