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Chapter 14

Case history: synthesis and decomposition of MTBE

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1. Introduction

Isobutylene is one of the four isomer mono-olefins with four carbon atoms (C_4 olefins), the others being 1-butene, 2-*cis*-butene and 2-*trans*-butene.

Olefins are not available in nature because oil and natural gas contain mainly alkanes, cycloalkanes and aromatics.

C_4 olefins are produced in two typical chemical processes: steam cracking and fluid catalytic cracking.

In these processes heavier hydrocarbons are cracked to lighter hydrocarbons.

C_4 hydrocarbons can be easily separated by distillation from heavier hydrocarbons in the effluents from these processes.

The stream obtained in this way comprises essentially C_4 olefins, normal butane, isobutane, butadiene (only in steam cracking effluents), and C_3 and C_5 hydrocarbons as impurities.

The content of isobutylene in this stream is 20–30% by weight in stream cracking effluents and 10–20% in fluid catalytic cracking effluents, depending on the feed and operating conditions.

There are some industrial processes (especially the production of synthetic rubbers) that require high purity isobutylene as feedstock (> 99.9%).

Herebelow are reported the normal boiling points and relative volatilities at 50°C of the various C_4 hydrocarbons:

	NBP	Relative volatilities
Butane	0.°C	0.886
Isobutane	− 12.°C	1.179
1-Butene	− 6.°C	1.041
2-*c*-Butene	+ 4.°C	0.805
2-*t*-Butene	+ 1.°C	0.847
Isobutylene	− 7.°C	1.059
Butadiene	− 4.°C	1.

It is impossible to obtain high purity isobutylene by distillation, because of the very small range of boiling points of the components (note especially that there is only 1 degree of difference between 1-butene and isobutylene).

A common separation scheme involves selective extraction with sulphuric acid: this scheme is very expensive and makes environmental concern.

The simplest alternative is the selective reaction of isobutylene with methanol to form MTBE, leaving unaltered the other hydrocarbons.

MTBE, after separation from the hydrocarbon mixture, can be decomposed into the reactants, allowing the recovery of pure isobutylene.

MTBE (methyl-*tert*-butyl-ether) is a compound with high octane number that has as-

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sumed a key-role in the elimination of lead from the gasoline pool: its world production has been dramatically increasing in the last years and is expected to increase further following new environmental rules in USA, imposing oxygenates in gasoline sold in highly polluted areas.

The scheme is thus composed by two subsequent steps: MTBE synthesis and MTBE decomposition.

2. MTBE synthesis

2.1. Conceptual design

The following reaction takes place:

$$\mathrm{i}-C_4H_8 + CH_3OH \leftrightarrow C_5H_{12}O(\mathrm{MTBE})$$

This reaction proceeds through the formation of carbocations on catalyst surface: the tertiary carbon atom in the molecule of isobutylene is much more reactive toward this type of reactions than primary and secondary carbon atoms in other C_4 hydrocarbons.

Anyway, small quantities of other ethers can be formed by *n*-butenes reactions with methanol, as detailed later.

So we can think to produce MTBE, and, after having purified it, perform the reversal reaction, decomposing it to methanol and isobutylene again.

With an easy separation, pure isobutylene can thus be obtained.

The same reaction must be performed forwards and backwards, in different conditions: being an equilibrium reaction, we must operate to shift the equilibrium in the desired direction.

The synthesis of MTBE is exothermic and thus thermodynamically favoured at low temperature; MTBE decomposition is therefore endothermic and favoured at high temperature.

This reaction is particularly influenced by the phase in which it is performed.

Its equilibrium constant, which is only a function of temperature, can be expressed in the following way:

$$K_{\mathrm{eq}} = \frac{C_{\mathrm{MTBE}}}{C_{\mathrm{ibte}} \cdot C_{\mathrm{Met}}} \cdot \frac{\gamma_{\mathrm{MTBE}}}{\gamma_{\mathrm{ibte}} \cdot \gamma_{\mathrm{Met}}} \qquad (1)$$

where C = concentration; γ = activity coefficient (a measure of non-ideality)

In liquid phase, the non-ideality of the mixture between methanol and hydrocarbons (at very low temperature two immiscible liquids are formed) increases very much the activity coefficient of methanol with respect to the vapor mixture.

Once the temperature is fixed, K_{eq} is a constant and therefore an increase in the denominator of (1) results in a corresponding increase of the term at numerator.

This means that, performing the reaction in the liquid phase, a much higher equilibrium concentration of MTBE can be obtained compared to the gas phase reaction: indeed from 5 to 70 times, depending on temperature.

The catalyst used for MTBE synthesis is a sulfonic acid resin, which is already active at low temperatures (40–50°C): so, it is sufficient to keep the reacting mixture at few atmospheres to perform the reaction in liquid phase.

Under these operating conditions, the equilibrium concentration of MTBE reaches very high values, with isobutylene conversion higher than 90%.

Now, let us try to determine the input–output structure of MTBE synthesis: there are two feeds (C_4 hydrocarbons and methanol), and surely one product (MTBE).

Then there will be a stream containing inert C_4 and some unreacted isobutylene: should it be recycled?.

Recycle is not worthwhile, because, due to the high conversion, this stream contains a very low amount of the reacting compound.

Furthermore, the recycle of such stream should be mainly a recycle of normal butenes, leading to higher formation of undesired byproducts, because a very high conversion of

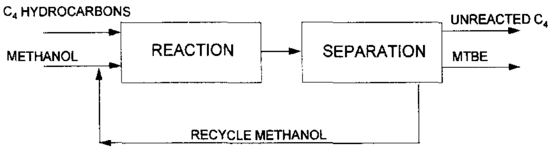

Fig. 1. Block diagram of the MTBE synthesis process.

isobutylene is obtained in the operating conditions chosen.

So, we decide not to recycle this stream (it goes to other refinery processes as for instance alkylation) and to recycle unreacted methanol.

We are also ready to use an excess of methanol to push isobutylene conversion, since isobutylene passes only once through the MTBE reactor.

The excess of methanol is limited by separation problems: as we shall see later, methanol forms low boiling azeotropes with C_4 hydrocarbons (containing 2–4% of methanol).

The azeotropic methanol is a limiting amount that can be easily separated from the mixture at reactor outlet.

The block diagram of MTBE synthesis is shown in Fig. 1.

Let us now examine the possible by-products:

1. Methanol can dehydrate to di-methyl-ether (DME):

$$2CH_3OH \rightarrow DME + H_2O$$

This is a non-equilibrium reaction and is kinetically favoured by high temperature, high concentration of methanol and low space velocity.

Its formation must be limited especially because it is a very volatile compound that leaves the process with the C_4 stream and is a poison in alkylation of C_4 hydrocarbons, a typical process downstream of the MTBE synthesis in refineries.

This is a constraint to work at high temperature and low space velocity.

2. The dimerization of isobutylene to give C_8 hydrocarbons is a non-equilibrium reaction favoured by low methanol concentrations and must be limited because dimers are heavy compounds that leave the process unit with MTBE decreasing its purity.

3. *tert*-Butyl-alcohol (TBA) is produced by isobutylene hydration:

$$i - C_4H_8 + H_2O \leftrightarrow TBA$$

This is an equilibrium reaction and is limited by the very low quantity of water present, and it is not worrying because TBA leaves the process with MTBE and by decomposition gives back isobutylene (it is indeed another industrial way to produce high purity isobutylene).

4. The reaction of methanol with normal butenes to give another ether: 2-methoxy-butane, an isomer of MTBE.

In the production of MTBE for gasoline blending this reaction is not important because 1-butene conversion is very low and the by-product is an ether, even if with a much lower octane number than MTBE.

In the integrated process of synthesis–decomposition, it becomes the key reaction, because 2-methoxy-butane cannot be separated from MTBE (exactly the same boiling point) and, in the subsequent decomposition section, decomposes to linear butenes that cannot again be separated from isobutylene and thus remain in the product: their allowed concentration in high purity isobutylene does not usually exceed 1000 ppm.

The equilibrium of this reaction is shifted towards the ether formation, but, in MTBE synthesis, it is limited by the competition of isobutylene: the tertiary carbon atom of isobutylene is much more reactive than the secondary carbon atoms of normal butenes, and reacts preferentially with methanol.

So, this reaction is kinetically limited, and is favoured by the same operating conditions that favour DME formation: in the combined process it sets the limit to the use of high temperatures and low space velocity.

2.2. The reaction section

The reactor will approach plug-flow, since it is an equilibrium limited reaction, and thus the concentration of the reactants (driving force to the reaction rate), is the highest possible in every point along the axis of the reactor.

The reaction is exothermic and therefore thermodynamically favoured at low temperatures: the highest conversion can be reached using a reactor that allows a low outlet temperature.

As discussed earlier, the multitubular reactor is what we are looking for: the reaction temperature is in a range that allows an external cooling with water.

Another advantage of isothermicity is the consistent reduction in by-products formation, because the mean reaction temperature is low.

Should a very high excess of methanol be used?.

The answer is no, because it favors DME and 2-methoxy-butane formation and gives separation problems.

In multitubular reactors, MTBE synthesis is usually operated with slightly over-stoichiometric methanol, or even slightly sub-stoichiometric in case of feeds with high concentration of isobutylene because dimers formation is anyway limited by low temperature.

A single multitubular reactor allows isobutylene conversions around 90%, because the excess of methanol is limited by its azeotropic amount with C_4 hydrocarbons.

To reach a higher conversion (98–99%), two reactors with intermediate separation must be used to shift thermodynamic equilibrium: if MTBE is later decomposed, it is not worth to push too much isobutylene conversion, to avoid 2-methoxy-butane formation: so, in synthesis–decomposition cycles the maximum isobutylene conversions of interest are about 96–97%.

If the feed is highly concentrated in isobutylene (40–50% as steam cracking feeds after butadiene extraction), a single reaction stage allows conversions of 90–93%, and a second reaction stage is necessary.

On the contrary, if the feed is diluted (20–30%), the desired conversion can be reached in a single stage.

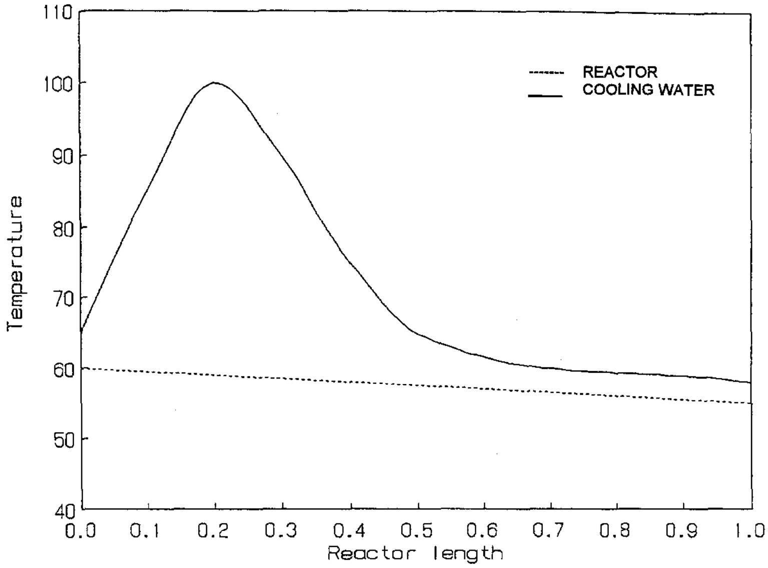

Fig. 2. Axial temperature profile in the MTBE synthesis reactor.

This is easily explained remembering that, as the feed is more concentrated, a lesser excess of methanol can be used (less inert hydrocarbons remain for the azeotrope).

The second reactor, in which thermal effects are very limited because isobutylene is highly diluted, will be of the cheaper adiabatic fixed bed type.

Another advantage of the multitubular reactor in the synthesis of MTBE comes as a consequence of the gradual poisoning of catalyst.

C_4 streams always contain impurities at the level of few ppm, like amides and nitriles, that deactivate the catalyst.

It is impossible to purify economically the feed from these impurities.

Tubular reactors can treat very well this slow deactivation, because temperature and flowrate of cooling water can be varied whenever necessary.

Such flexibility is not allowed by adiabatic reactors.

Properly speaking, the multitubular reactor is not really isothermal: in fact, at the entrance of the tubes, where concentration of the reactants is maximum, the heat generated by the reaction cannot be totally transferred to the cooling water (Fig. 2), and thus a peak of temperature is formed; then, as soon as equilibrium is approached, reaction becomes slower and temperature begins to decrease approaching cooling water temperature at the outlet.

The zone of the temperature peak is the one that gives most of the conversion: as the catalyst deactivates, the peak of temperature moves toward the exit of the tubes.

When the final part of the tube begins to be interested by the peak, it is time to change the catalyst.

2.3. The separation section

Now some words about separation: the same problems will be found again in the decomposition section because the same components are involved.

First of all the choice of pressure: it must be the minimum pressure to condense C_4 hydrocarbons with cooling water (35–40°C), without using expensive refrigerant cycles: a higher

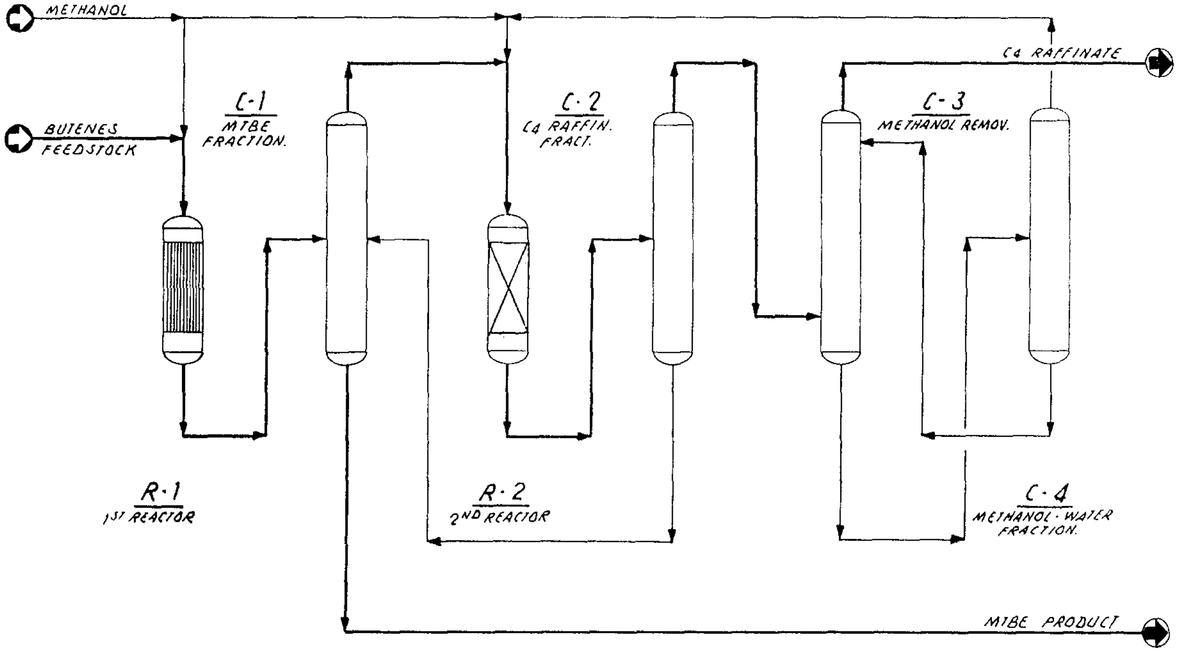

Fig. 3. Process scheme of MTBE synthesis.

pressure is not used because the relative volatilities of the compounds diminish increasing pressure making separation more difficult.

According to their boiling points, we should expect to separate methanol as a residue, C_4 as a distillate, and MTBE as distillate or residue in a second distillation tower.

However, as told before, the liquid mixture is highly non-ideal: as a consequence it forms azeotropes.

Precisely, a methanol–C_4 azeotrope is formed, with the lowest boiling point, containing about 3% of methanol; a methanol–MTBE azeotrope is formed, too, with an intermediate boiling point and MTBE becomes the heaviest compound.

The distillation is performed to have hydrocarbons with the azeotropic methanol as distillate, and MTBE as residue.

So, the maximum excess of methanol in the reactor is the quantity that can be distilled as azeotrope with the C_4.

If more methanol is present, the methanol–MTBE azeotrope is formed: it can be distilled or left as residue, but in this case a new separation between methanol and MTBE is needed.

Of course, this separation cannot be a simple binary distillation, but a third compound should be involved to avoid the azeotrope.

Using two reactors, the distillate, additioned with fresh methanol, is the feed to the second reactor, while the residue is the product stream.

A strong excess of methanol is used in the second reactor, because now there is only a small percentage of isobutylene in the C_4 stream: its azeotropic quantity is much higher than the one necessary to react stoichiometrically with isobutylene.

The following distillation will give again the methanol–C_4 azeotrope as distillate, and MTBE as residue, that can be recycled to the first distillation tower.

The scheme of MTBE synthesis is shown in Fig. 3.

Finally, a last operation must be done: methanol, to be recycled to the reactors, must be separated from C_4 hydrocarbons.

This separation is performed exploiting the different chemical features of these components: methanol is a polar compound, completely soluble in water, while hydrocarbons are immiscible with the same.

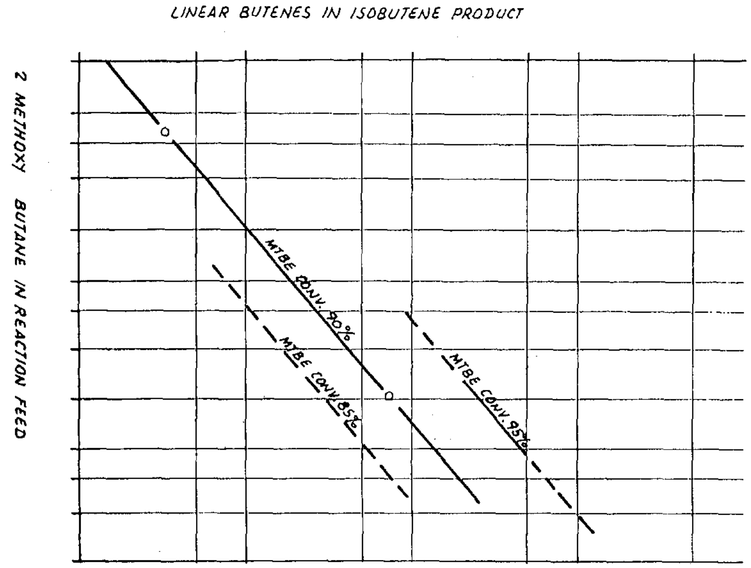

Fig. 4. Concentration of *n*-butenes in the product vs. concentration of 2-methoxy-butane in the feed.

Water is then used as solvent and the resulting methanol–water mixture is easily separated by distillation.

3. MTBE decomposition

3.1. Conceptual design

The decomposition of MTBE must be operated in vapor phase, since we have seen the effect of the non-ideality of the liquid mixture on equilibrium conversion.

Since the reaction is endothermic, it will be performed at higher temperature than MTBE synthesis.

Since we are dealing with a vapor phase reaction causing an increase in the overall number of moles, the high pressure adversely affects thermodynamic equilibrium.

Consequently, reaction pressure will be the minimum necessary to condense the reaction product with cooling water, to avoid to compress the effluent gases.

The catalyst used for MTBE decomposition is based on silica.

2-Methoxy-butane has the same boiling point as MTBE, so these two compounds cannot be separated: if undecomposed MTBE is recycled, also 2-methoxy-butane recycles and builds-up in the cycle.

The higher the 2-methoxy-butane concentration in the cycle, the higher its concentration in the decomposition reactor feed and the higher its decomposition into methanol and normal butenes, resulting in an increased percentage of linear butenes in the product, that eventually can go beyond the specifications.

The only viable solution is a purge on the recycle: this means that some MTBE must be purged, too.

In Fig. 4 the concentration of linear butenes in isobutylene produced is reported versus the concentration of 2-methoxy-butane in the cycle for different MTBE conversions: it can easily be seen how high MTBE conversion and high 2-methoxy-butane build-up affect the purity of the product.

Unfortunately, to avoid excessive loss of MTBE, a fairly high concentration of 2-methoxy-butane in the cycle must be reached: the best compromise must be reached between purity of the product and loss of MTBE.

In Fig. 5 the equilibrium conversion is shown

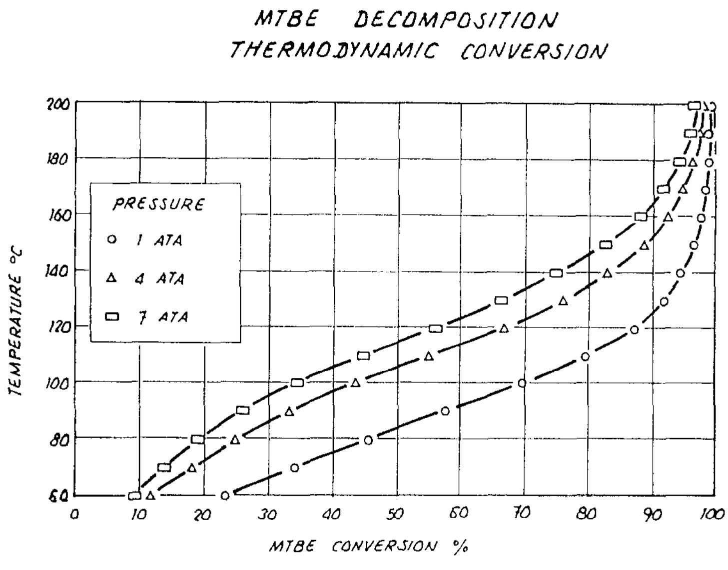

Fig. 5. Thermodynamic conversion in MTBE decomposition.

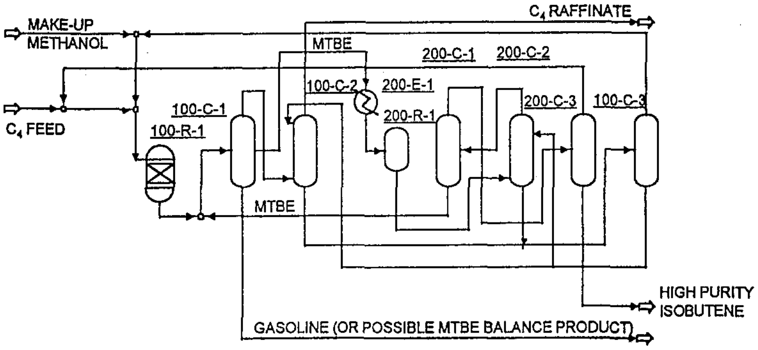

Fig. 6. Overall process scheme: alternative 1.

as a function of temperature and pressure: a temperature of 140–150°C must be reached to have a conversion around 80%: decomposition is not pushed further to avoid excessive decomposition of 2-methoxy-butane.

With 80% decomposition of MTBE, 2-methoxy-butane builds-up in the feed to decomposition to a level such that the linear butenes in the product are largely below 1000 ppm.

The recycle of undecomposed MTBE can be avoided if the plant is integrated in a refinery or MTBE can be sold to a refiner as octane enhancer.

About the other by-products, TBA decomposes to isobutylene and water, and the same reactions than in MTBE synthesis are present.

DME is also formed in the final part of the reactor where a high partial pressure of methanol is reached: its allowable concentration in high purity isobutylene is usually of 10 ppm, so that it must be separated from the product.

3.2. Reaction and separation

How shall the decomposition be performed?

Also in this case plug-flow and a careful control of temperature are needed: in fact, being the reaction endothermic, if temperature becomes too low along the reactor, condensation can begin, and fluid–dynamic problems can arise, together with loss of conversion and tar formation on catalyst surface.

So, a tubular reactor is used also in this case, with condensing steam as heating medium: the temperature is regulated by the steam pressure.

In the separation section, the main difference with respect to the separation following MTBE synthesis is in the high amount of methanol present.

A separation by distillation of pure MTBE as residue and the azeotropic methanol–isobutylene mixture is not possible anymore.

All the methanol in excess will remain with

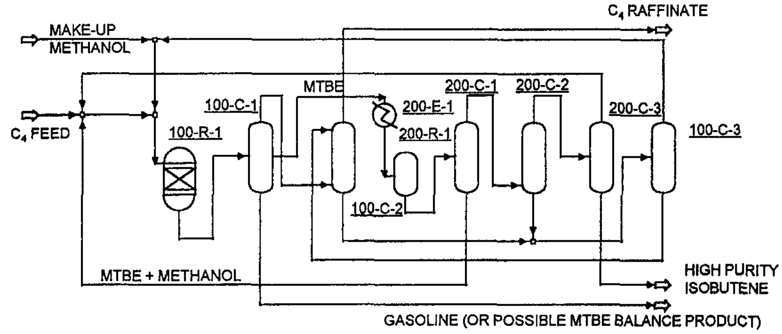

Fig. 7. Overall process scheme: alternative 2.

MTBE as residue: indeed methanol represents more than 60 mol% of this mixture.

Such mixture cannot be recycled to the decomposition reactor, because methanol is now a product and must leave the decomposition section, and cannot be recycled to a distillation column in MTBE synthesis because the excess of methanol will again affect the separations.

Recycle is only possible to the MTBE synthesis reactor, even if the presence of MTBE will slow the reaction rate and lower the conversion of isobutylene: this is anyway done and the separation is operated to keep some isobutylene as residue, too, to avoid a loss of purity in the top product.

The azeotropic mixture is separated by water extraction in the same way than in MTBE synthesis.

A second possibility in separation is to perform the water extraction directly downstream of the reactor: the resulting water–methanol mixture is sent to the distillation already present in MTBE synthesis and methanol is recycled to the synthesis reactor.

MTBE and isobutylene are easily separated by distillation, and MTBE can be recycled directly to the decomposition reactor (or to a distillation column in MTBE synthesis).

Such a scheme is used when very high isobutylene conversions are needed, even if it is much more expensive from the energetic point of view because a bigger amount of methanol must be reboiled.

The two overall schemes are reported in Fig. 6 and Fig. 7.