

## Phase equilibria of alkanol/alkane mixtures in new oil and gas process development

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**Abstract** - With the reduction of lead in gasolines, a growing number of processes in which alkanols and alkanes co-exist to produce oxygenated additives for gasolines are under development or have already reached the industrial production stage. In the processes selected the knowledge of the alkane/alkanol equilibria is essential for the separation techniques to be applied : azeotropic distillation of ethanol or higher alkanols, liquid phase methanol process, solvent extraction of fermentation products, azeotropic and catalytic distillation of methyl ethers. Likewise, due to antihydrate properties, absorption of sour gases and immiscibility with alkanes at low temperature, methanol could play a more important part in natural gas processes. Without claiming to make an exhaustive review of all the processes of the refining and gas industries where alkanols and alkanes are co-existing, it appears clear that methanol, ethanol, methyl ethers and to a lesser degree mixtures of higher alkanols will be used on a larger scale. This development will inevitably be accompanied by a new demand for models that can simulate equilibria involving polar components such as alkanols mostly under severe operating conditions ; for example equilibria at low temperature and high pressure, in the presence of water and with the possibility of liquid/liquid demixing. The process engineer is particularly fond of predictive models that offer powerful (albeit sometimes unreliable) tools for designing new plants. The concomitant development of sophisticated models fitted to experimental data and of predictive models will always be a major research objective.

### INTRODUCTION

With the development of computers, simulation has assumed a dominant role in process design. To be reliable, however, simulation must make an accurate representation of the phase equilibria in the entire range of operating conditions of the process. While simple models, based on the concept of corresponding states, are satisfactory for the thermodynamic description of mixtures containing compounds of comparable structures, implying minor deviations from ideal conditions, it is often necessary to use more complex models to describe systems involving components of very different types, highly polar, sometimes with a wide deviation from the ideal state, and liable to form azeotropes and/or to produce liquid/liquid separation.

Alkanol/alkane mixtures in particular are among the systems that are difficult to represent over a wide range of pressures and temperatures. A breakthrough was achieved by the use of equations of state with mixing rules derived from activity coefficient models used for representing the non-ideality of the liquid phase under low pressure : NRTL, UNIQUAC (Ref. 1, 2). This need for models is especially strong because oxygenated products are likely to assume a top role in the refining industry with the progressive elimination of lead in gasoline.

The alkanols, especially methanol and ethanol, can be used to boost the octane number. The use of methanol entails the need for the addition of a co-solvent (higher alcohols) to avoid the settling of an aqueous phase in the tank due to a drop in temperature. Methanol, the cost of which fluctuates at the level of the price of premium grade gasoline, also presents the drawback of increasing the vapor pressure of the gasolines due to the existence of azeotropes with the hydrocarbons. Ethanol, although not competitive with methanol, may be preferable for political and economic reasons of energy self-sufficiency or for the use of surplus agricultural materials containing sugars, starch and cellulose, or for a local installation at the farm to supply the needs of farm machinery. In Brazil, for example, cars run on partly dehydrated ethanol containing 4 to 8% by weight of water, subject only to minor engine adjustments. To avoid these changes, the European Common Market plans to use

mixtures containing less than 10% oxygenated products, such as the M3TBA2 mixture (3% methanol + 2% ter-butyl alcohol). However, other co-solvents, such as a mixture of acetone/1-butanol/ethanol or a mixture of higher alkanols than methanol, have been one of the major research objectives in recent years, and could be resorted to in the event of another sharp rise in the cost of crude oil. Instead of methanol mixed with various co-solvents, methyl esters already play a significant role as additives for unleaded gasolines.

In this context, many research projects are directed at the improvement or optimization of oxygenated additives production and purification processes that are already commercialized or at the development of new synthesis methods or new purification techniques including:

- . production of dehydrated ethanol,
- . production of methanol from synthesis gas,
- . production of a mixture of heavy alkanols from synthesis gas,
- . production of a butanol/acetone mixture from fermentation,
- . production of methyl ethers.

In the examples listed, the modelling of alkane/alkanol equilibria is often a decisive factor for process control. Depending on each situation, the hydrocarbons concerned play the role of an entrainer in azeotropic distillation or a selective extraction solvent, or even of a heat transfer fluid. This list is incomplete and, in particular, it fails to consider processes in which n-alkane and alkanol co-exist because either or both are minor by-products of the reaction or feedstock impurities without any significant effect on the operation of the process. For example, the Fischer-Tropsch processes, which yield gasolines or gas oil from the  $\text{CO} + \text{H}_2$  mixture and also produce a low proportion of alcohols, are not considered.

The gas industry also makes substantial use of methanol as a polar solvent, not only for its ability to absorb sour gases ( $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ), but also for its pronounced antihydrate effect.

The production of oxygenated additives for unleaded gasolines and the use of methanol in natural gas processes will be dealt with in succession, in order to highlight the importance of modelling alkane/alkanol equilibria for the development of the processes concerned. In this respect, we shall also discuss the work carried out at Institut Français du Pétrole in the past ten years.

## PRODUCTION OF OXYGENATED ADDITIVES FOR MOTOR FUELS

### Ethanol

Ethanol produced by the hydration of ethylene or by fermentation is obtained diluted in water, so that its addition to gasolines requires dehydration to avoid the use of a co-solvent.

As ethanol and water form an azeotrope containing 96% by weight of ethanol, dehydration takes place in two steps. The first step produces preconcentrated ethanol, generally in the azeotropic composition.

Setting aside the molecular sieve adsorption and pervaporation techniques that are only developed for small capacity plants, the second step makes use of a third component, an entrainer, in an azeotropic distillation process. Chawla (ref. 3) selected twelve potential entrainers of which the list is given in Table 1. Benzene and cyclohexane are now in routine industrial use. Among the other hydrocarbons mentioned are two n-alkanes: n-pentane and n-hexane. Like the foregoing compounds, these were selected for the following properties:

- . total miscibility with the ethanol/water feed,
- . formation of at least one binary heteroazeotrope with water at minimum temperature,
- . formation of a ternary azeotrope at minimum temperature,
- . chemical stability.

TABLE 1. List of entrainers in azeotropic distillation of ethanol

benzene	n-hexane
cyclohexane	2-methylpentane
n-pentane	hexene-1
cyclopentane	diethylether
methylcyclopentane	2,2-dimethylpentane
isopentane	2,2,3-trimethylbutane

Source: Chawla (ref. 3)

The shape of the resulting ethanol/water/entrainer ternary diagram is shown in Fig. 1.

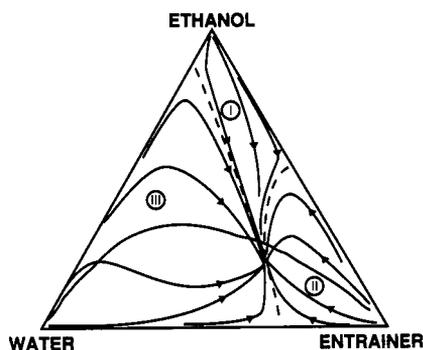


Fig. 1. Distillation path of ethanol-water-entrainer system

The distillation paths converge towards the ternary heteroazeotrope which has the lowest temperature so which is produced as a vapor distillate in the first column. As it cools, this vapor settles in two liquid phases. The entrainer-rich phase is refluxed while the ethanol is produced at the column bottom. The aqueous phase is fed to a second column which extracts the water and recycles the residual ethanol and entrainer. Although a large number of variants exist, a conventional process flow sheet is shown in Fig. 2. The simulation of the process relies on a reliable representation of the ternary demixing zone. Under low-pressure conditions, a heterogeneous model that uses an activity coefficient model (for example, NRTL or UNIQUAC) generally allows an accurate representation of mixtures containing polar components. For mixtures leading to liquid/liquid demixing, however, the regression of the model parameters must represent not only binary liquid/vapor equilibrium, but also binary and ternary liquid/liquid data. If benzene is used as an entrainer, a comparison of the modelling by NRTL (ref. 4) with the experimental results is shown in Fig. 3. The results are satisfactory even if the slope of the equilibrium lines is not perfectly calculated, especially in the upper part of the demixing zone. This means that the simulation results show good agreement with the specifications obtained on ethanol for industrial processes with benzene (or cyclohexane). However, Chawla (ref. 3), Rolat (ref. 5), Keister (ref. 6) and Magnussen (ref. 7) emphasize the difficulty of convergence of the computation algorithms, which lead to a multiplicity of solutions. Magnussen (7) also proposes the use of the UNIFAC model based on the concept of group contribution to predict the liquid phase activity coefficients in the representation of liquid/vapor equilibria. However, the extension of the use of the UNIFAC model to the liquid/liquid region can be very unreliable if the group interaction parameters are not themselves obtained from experimental liquid/liquid data. Hence additional liquid/liquid experimental data or two sets of parameters become necessary to provide a more reliable result.

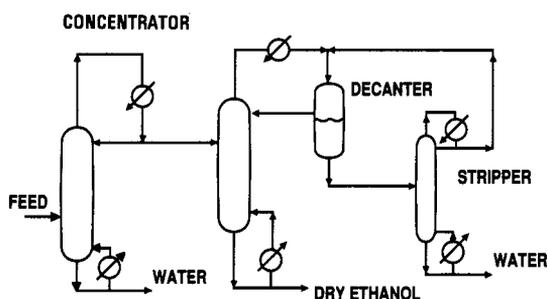


Fig. 2. Conventional process for ethanol dehydration

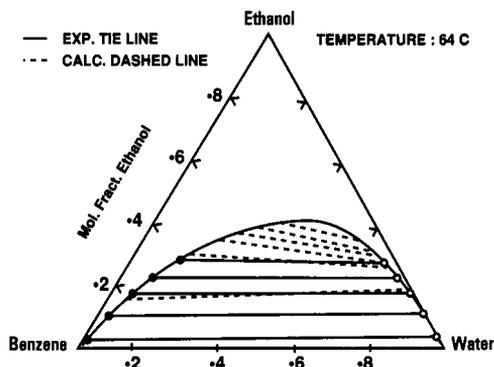


Fig. 3. Isothermal liquid-liquid equilibria benzene-ethanol-water system

Ref. Morachevsky and Coll., *Ves. Lening. Univ. Fiz Khim*, 13, 4 (1958)

Faced with the scarcity of experimental equilibrium data for entrainers other than benzene and cyclohexane, Chawla (ref. 3) proposed using the predictive character of the UNIFAC model to make a preselection of the best entrainer. According to Black (ref. 8) n-pentane should be preferable to benzene and to diethylether, particularly for reasons of energy savings. As a denaturing agent, n-pentane can be left in substantial amounts in the dehydrated ethanol and mixed subsequently with the gasoline. The use of a  $C_5-C_8$  cut directly produced at the

refinery may represent an additional asset. Given the large number of components in the entrainer, modelling requires the correlation of the parameters obtained by regressing a very large number of binary and ternary liquid/vapor and liquid/liquid equilibrium points. Black (ref. 9) simulates the dehydration of ethanol using a mixture of eleven major hydrocarbons from isopentane to n-octane as entrainer. The modelling of the phase equilibria by the modified Van Laar method leads to a gain in energy with respect to the process using a conventional entrainer, but there is no possible comparison to experimental operation.

IFP has undertaken experiments in a laboratory unit to evaluate the performance of a process using a gasoline as the entrainer and to identify potential foaming or phase coalescence problems in the decanter. Due to the additional reflux that inevitably occurs in small non perfectly adiabatic columns, the value of the minimum reflux necessary for a given water specification of the ethanol produced can not be accurately determined. This value could be obtained by simulation if an efficient model is available for representing the non-ideality of the liquid phase, and if the entrainer can be reduced to a limited number of key components for computing the equilibria.

With the aim of supplying ethanol for fuel, the use of a heavier hydrocarbon cut has also been proposed as a selective solvent for extracting alcohol from aqueous solution. The process developed by Intertechnology Solar Science Applications Inc, USA (ref. 10) simply recover the solvent by lowering the temperature. According to the process flow sheet shown in Fig. 4, the wine produced by fermentation is pre-concentrated to about 30% by weight and then subjected to liquid/liquid extraction by a light paraffinic oil at 105°C. The extracted phase cooled to 30°C settles in an alcohol phase containing 4 to 5% by weight of hydrocarbon, which can be added directly to the automotive fuels, and a solvent phase recycled to the extractor, with make-up to account for losses. The absence of accurate data concerning the paraffin/ethanol/water equilibria in the extraction and demixing separation conditions precludes any conclusions on the actual energy performance of the process. However, it is probable that the high solvent ratio required will raise the investment cost considerably.

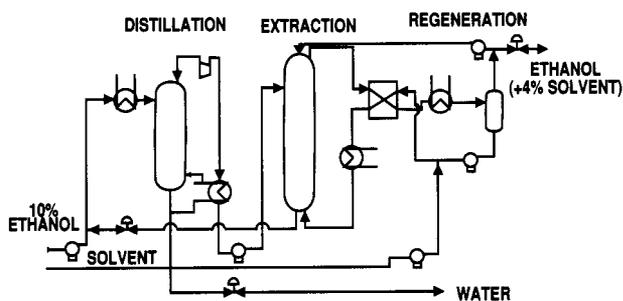


Fig. 4. Dehydration of ethanol by solvent extraction (ITC/SAI)

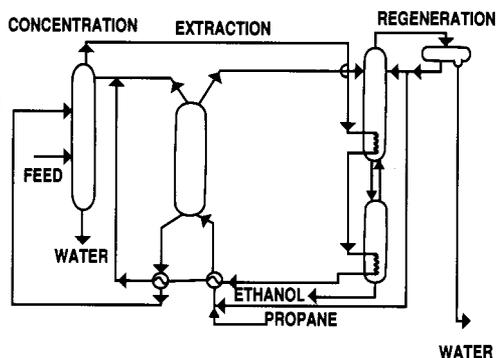


Fig. 5. Dehydration of ethanol with propane (IFP)

IFP recently patented (ref. 11) a low-energy and economical investment process that combines extraction with distillation, by using the same solvent as an extraction agent and as an azeotroping agent. The solvent, after extracting the ethanol under pressure, is regenerated by distillation, which also allows the recovery of the residual water by phase splitting in the reflux drum. Thus the purity of the ethanol produced may exceed 99.5 wt %. The solvents considered are light n-alkanes, preferably propane or butane, as supplied at the refinery. The flow sheet, shown in Fig. 5, includes the following essential steps.

. Preconcentration of ethanol by distillation.

. Liquid/liquid or liquid/fluid extraction, if the solvent is raised to pressure and temperature conditions higher than those of its critical point. An extraction yield of 95% is preferable due to the concomitant solvent savings. However, the overall dehydration yield is very close to 100% since the incompletely purified raffinate phase is recycled.

. Solvent regeneration, which simultaneously terminates the dehydration of the alcohol. In order to recover the heat made available by the condensation of vapors produced by the preconcentration step, it is preferable to operate with two columns at two distinct pressure levels. The water which forms an azeotrope with the solvent is produced in the vapor at the top of the first column. It settles in the reflux drum, where it can be withdrawn, while a significant proportion of solvent is left in the ethanol produced at the column bottom. The second column, which operates at lower pressure, completes the hydrocarbon/alcohol separation.

In the development phase, simulation is a useful tool for calculation of the material balances for the overall process, including recycles, without the need for building a laboratory pilot plant. Faced with the difficulties raised by the modelling of the pressurized extractor, the distribution coefficient obtained from interpolation of several equilibrium experimental data at various temperatures and pressures was employed. In designing new processes, the combination of a model with experimental results leads undoubtedly to a compromise between simplicity and accuracy.

## Methanol and alkanol co-solvents

### Methanol

Another alternative of oxygenated additives for motor fuels consists in using methanol obtained from synthesis gas,  $\text{CO} + \text{H}_2$ , which is itself mainly obtained from natural gas or coal.

The highly-exothermic reaction:



is favored, at the thermodynamic equilibrium, by low temperature and high pressure. The well known ICI (Imperial Chemical Industries) process controls the temperature (about 270°C) by the injection of quenching gas. Processes under development (Aker, Chemical Systems, IFP) are aimed at the production of methanol in the liquid phase. The objective is to use a heat transfer liquid to remove the heat of reaction.

The main selection criteria for the heat transfer fluid are:

- . good chemical stability in the reaction conditions,
- . low vapor pressure,
- . low solubility for methanol and water

The choice is a heavy paraffinic cut, such as a mixture of normal alkanes from  $\text{C}_{12}$  to  $\text{C}_{18}$ . Figure 6 shows a flow chart of the fractionation of the reactor effluents.

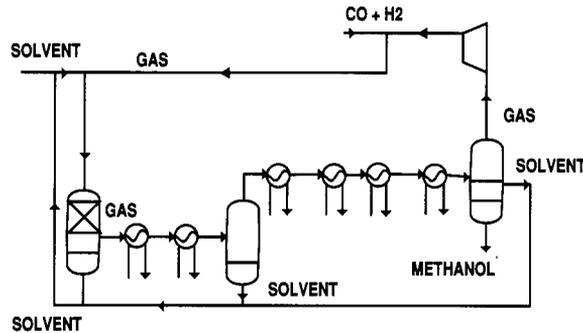


Fig. 6. Separation of effluent of liquid phase methanol process (IFP)

Most of the heat transfer fluid that does not participate in the reaction is recovered in the liquid phase at the reactor exit and is recycled. The vapor phase draw off in equilibrium with this solvent phase in the reaction conditions still contains hydrocarbon vapors that must be removed. Cooling by a progressive lowering of the temperature first achieves a simple condensation of solvent in the first separator tank. The subsequent condensation of methanol causes a separation by methanol/solvent demixing in the second separator tank, while the gas phase, mainly containing the unconverted  $\text{CO} + \text{H}_2$  mixture, is recycled. The methanol produced must still undergo a final purification step to remove the main impurities: dissolved gas, water, hydrocarbons, higher alcohols. According to the purification step flow diagram, a first column removes the compounds more volatile than methanol, and a second the less volatile components. Water is extracted at the bottom of the second column, and pure methanol at the top, while the hydrocarbons and higher alcohols which have intermediate volatilities due to the formation of heteroazeotropes with water are drawn off in a side stream.

To represent the equilibria correctly, the presence of components at supercritical conditions ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{H}_2$ ) requires the use of an equation of state. The additional presence of polar compounds (methanol and water) and of hydrocarbons requires the choice of a reliable mixing rule derived from activity coefficient models. Much remains to be done, both in terms of model performance and computation algorithms, to achieve an accurate representation of the liquid/vapor and liquid/liquid/vapor equilibria involved in the multistage condensation of methanol.

### Alkanol co-solvents

Methanol, even totally anhydrous, is not soluble in all proportions and at all temperatures in all gasolines. In fact, motor fuels and highly-hygroscopic methanol always contain traces of water which further accentuate the tendency towards demixing. The cloud point of a gasoline is the temperature at which this demixing is initiated. The cloud point can be determined experimentally, for example, by observing the diffusion of light through an equilibrium cell.

The accurate modelling of hydrocarbon/methanol equilibria in the presence of small amounts of water would be extremely helpful for selecting the best co-solvent, and would avoid the need for systematic experiments. All simple alkanols, particularly ethanol, can perform this role. However, the co-solvent power increases with the chain length, so that is preferable to use heavier alcohols; tert-butyl alcohol (TBA) co-produced in the synthesis of propylene oxide, is the most widely used. Yet mixtures of higher alkanols, such as those obtained from synthesis gas or by butyl fermentation, could perform this role.

### Mixtures of higher alkanols from synthesis gas

The catalytic processes under development, including the IFP process (ref. 12) and the competing Dow Chemical (ref. 13) and SNAM Progetti (ref. 14) processes, produce a mixture containing 55 to 65% methanol, 35 to 45% of different  $C_2$  to  $C_6$  alkanols, and traces of hydrocarbons and water that must be removed.

As for ethanol dehydration, azeotropic distillation with benzene has been suggested (ref. 12). The flow sheet, shown in Fig. 7, includes a preliminary demethanolization step, where methanol, which does not form an azeotrope with water, is separated by distillation. The two additional azeotropic distillation columns allow the dehydration of the alcohols containing at least two carbon atoms. The NRTL model has successfully reproduced the results of experimental operation in the laboratory.

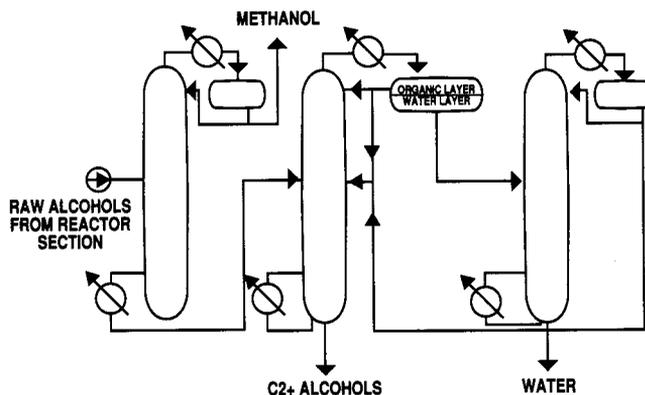


Fig. 7. Heteroazeotropic distillation of higher alcohols from syngas (IFP)

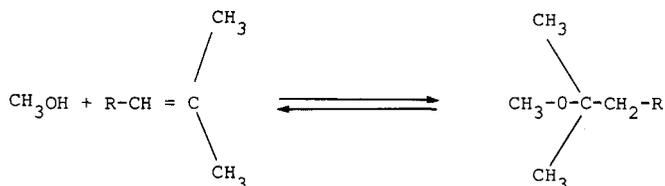
IFP has also patented a technique that combines extraction with distillation by the preferential use of propane or butane as an extraction agent and azeotroping agent. The flow sheet, which includes a preliminary demethanolization step, is shown in Fig. 8. If the water content of the reaction effluent is low, it is preferable to eliminate the extraction step.

### Acetone/butanol/ethanol (ABE) mixtures from fermentation

Butyl fermentation produces a mixture containing 2% by weight ABE in water, with the ABE mixture consisting of approximately 40% acetone, 50% 1-butanol, and 10% ethanol. For use with motor fuels, an extraction process by a gasoline cut could compete with a more conventional distillation process. A preliminary preconcentration step serves to leave the solids in suspension in the water to carry out the extraction on a clean feed. However, the low solvent power of the gasolines for alkanols with a short hydrocarbon chain is a major drawback. Simulation should help to develop other more competitive variants, such as the prior distillation of acetone and ethanol, followed by the extraction of 1-butanol with gasoline, that could significantly reduce the amount of solvent required for the process.

## Methyl ethers

Like alkanols, methyl ethers can be used to boost the octane number of unleaded gasolines, and do not need the supplementary addition of co-solvents. MTBE\* and TAME\* are obtained by the reaction of methanol with gaseous olefins contained in a C4 cut or, respectively, a C5 cut produced by catalytic cracking or steam cracking, by the reversible reaction:



The purification step removes the residual hydrocarbons and methanol. In the MTBE synthesis, the hydrocarbons mainly contain alkanes, n-butane and isobutane, and olefins 1-butene and 2-butene, because excess methanol helps to consume nearly all the isobutene (2-methylpropene). In fact, the methanol/butane mixtures that form azeotropes whose boiling points are lower than that of the methanol/MTBE azeotrope can be recovered at the top of the distillation column. This column operates under pressure to avoid the use of a refrigerant cycle in the top condenser. The pressure is then adjusted between 5 and 15 bar to carry off the methanol with the n-alkanes, taking account of the increase in the methanol content of the azeotrope with pressure. As shown in Fig. 9, the IFP process (ref. 15) includes a supplementary water wash section to recover the methanol, followed by fractionation of the methanol/water mixture.

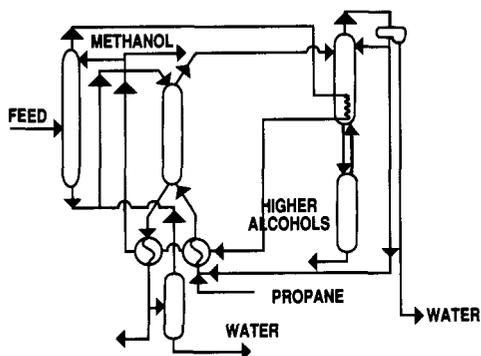


Fig. 8. Dehydration of higher alcohols from syngas with propane (IFP)

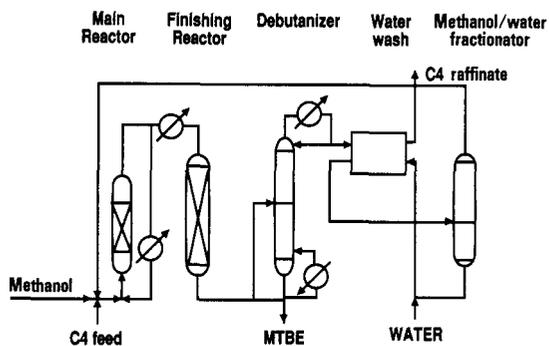


Fig. 9. MTBE process (IFP)

IFP recently developed a more efficient MTBE synthesis process that uses the CRL (Chemical Research and Licensing) reactive distillation technology (Fig. 10). The objective is to increase the degree of advancement of the reaction in accordance with the principle of Le Châtelier. Two strategies are available, depending on whether the operation is carried out with slight excess methanol with respect to stoichiometry, that serves to recover 1-butene free of isobutene, or with a slight under-stoichiometric level of methanol, to eliminate the methanol washing section and the final fractionation of the methanol/water mixture (ref. 16, 17).

In the production of TAME, the ether is generally not separated from the unreacted hydrocarbons and is incorporated as such in the motor fuels.

## METHANOL IN THE TREATMENT OF NATURAL GAS

Before any use, and especially for its chemical upgrading to alkanol, natural gas must be rid of a number of undesirable components, including  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$ , to make it transportable without the risk of corrosion or the formation of a solid phase (ice, hydrate), or simply for safety considerations.

Two alternatives are generally applied:

- . in-line injection of antihydrate, glycol or methanol, up to the treatment plant,

\* MTBE is 2-methoxy-2-methylpropane and TAME is 2-methoxy-2-methylbutane.

. treatment prior to transport, including the successive steps of sweetening, dehydration and recovery of liquid hydrocarbons.

For a gas that contains practically no  $H_2S$  or with a limited acid gas content, the sweetening step can be eliminated. The gasoline extraction step is also unnecessary in the case of two-phase transport

As an example, Fig. 11 (ref. 18) shows a flow chart in which methanol is used to dehydrate natural gas, combined with LPG recovery.

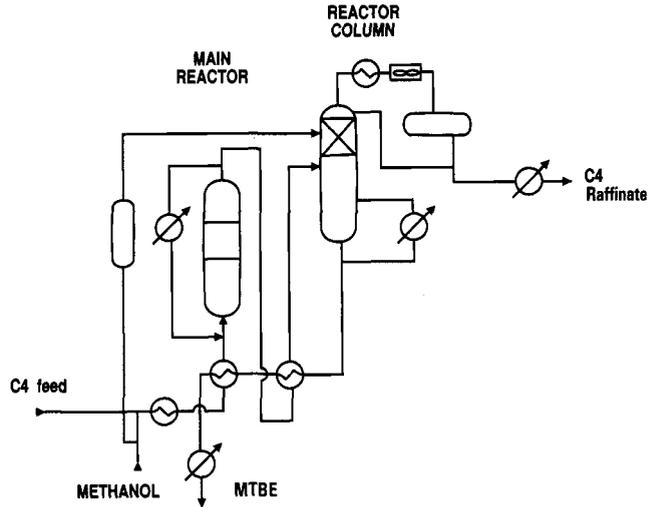


Fig. 10. MTBE process with catalytic distillation (IFP/CRL)

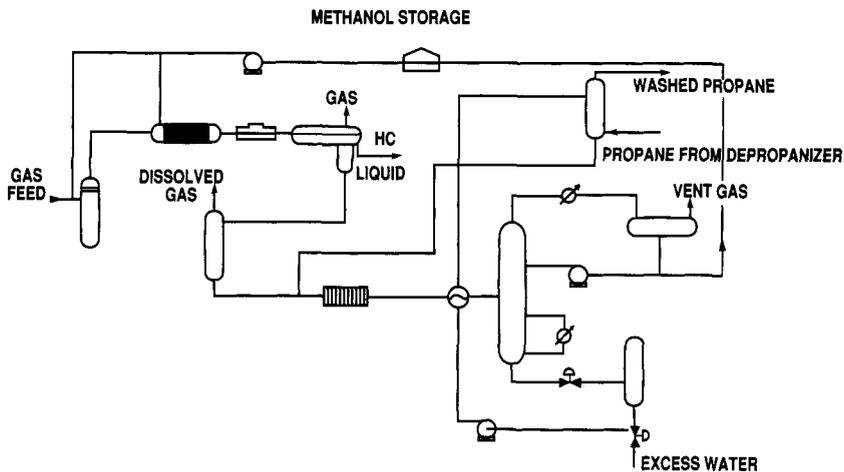


Fig. 11. Inhibition of hydrate formation by methanol injection

IFP is developing a new process to achieve a gain in investment, which is more compact and performs the three steps simultaneously by the implementation of a physical solvent at low temperature. It will cover a wide range of applications, especially offshore, and should thus promote the development of many gas and associated gas fields. In this new process, methanol is preferable for the following properties.

### Antihydrate property

The proportion of inhibitor to be injected can be calculated from nomographs or from the Hammerschmidt formula. Nevertheless, at equivalent density, gases of very different compositions can lead to hydrate formation pressures that are quite different from those calculated. The use of less empirical methods that use equations of state in computer programs is a definite improvement (ref. 19, 20).

### Physical absorption of sour gases

Methanol is one of the physical solvents that is competitive with chemical absorption processes by alkanolamine-type solvents, which are energy-consumer for regeneration. The Rectisol methanol absorption processes developed by Lurgi Linde have found their main applications on gases produced by coal gasification (SASOL) or gases with a very low content of hydrocarbons heavier than methane. In fact, if this condition is not satisfied, the absorption of the sour gases produces a significant co-absorption of  $C_2+$  hydrocarbons. To recover these hydrocarbons, it is therefore necessary to use a subsequent separation train that is problematic due to the presence of  $CO_2/C_2$  or  $H_2S/C_3$  azeotropes.

### Immiscibility with hydrocarbons at low temperature

The immiscibility of  $C_3+$  hydrocarbons with methanol at low temperature allows easy recovery of LPG. The additional presence of water dissolved in the solvent increases this tendency towards demixing.

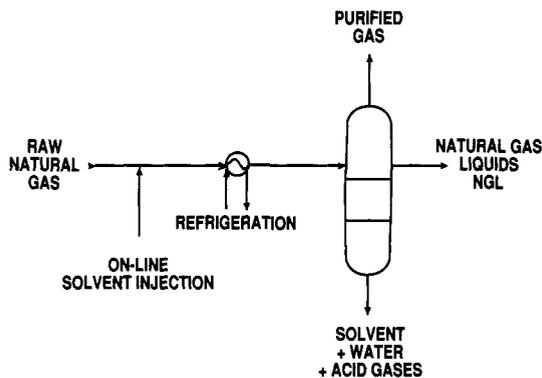


Fig. 12. Schematic flow diagram of the integrated process (IFP)

The schematic flow chart of the IFP integrated process under development is shown in Fig. 12. The lowering of the temperature in the presence of methanol causes separation into three phases without hydrate formation: an upgradable liquid hydrocarbon phase, a dehydrated, heavy hydrocarbon-free gas phase, and a solvent phase containing the water to be sent to regeneration. In a supplementary step, methanol can be used in larger amounts to absorb the sour gases. The precise knowledge of the three-phase equilibrium in the separator tank is necessary to evaluate the performance of the process, and especially to determine the methanol losses in the gas phase and the solubility of the sour gases and of the methanol in the liquid hydrocarbon phase. One problem in this area is the scarcity of published liquid/vapor, liquid/liquid, and liquid/liquid/vapor equilibrium data. The acquisition of accurate experimental phase equilibrium data at low temperature is a difficult problem that must first be resolved. The subsequent simulation of the process will depend on the performance of the model in representing these data. So far the combination of an equation of state with activity coefficient models remains a reliable way for the representation of mixtures partly consisting of supercritical components and a polar solvent such as methanol.

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