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CATACOL™, A LOW COST REACTIVE DISTILLATION TECHNOLOGY FOR ETHER PRODUCTION AND FOR REVAMPING EXISTING UNITS

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MASTER

SUMMARY

IFP has developed a new reactive distillation system. This system is named Catacol™. In addition to overcoming equilibrium limitations, Catacol™ minimizes catalyst costs because, contrary to other catalytic distillation systems, Catacol™ does not require proprietary internals or catalyst packaging. Although recently marketed, four applications of Catacol™ for MTBE production will be on-stream in the near future, thereby substantiating the competitiveness of this technology. Catacol™ can be applied to a number of types of processes, for example etherification or hydrogenation. Catacol™ is also well suited for the revamp of existing units.

ABSTRACT

This paper outlines the advantages of Catacol™ and describes this new technology. Some applications of Catacol™ such as debottlenecking of existing etherification units are developed. Technological considerations for the production of ETBE are also provided in this paper and the conversion of MTBE plants to ETBE manufacture is addressed.

1. INTRODUCTION

Ethers are the main oxygenated compounds used in gasoline, because they have physical properties close to those of hydrocarbons. In addition to their high octane numbers ethers have been shown to control CO emissions, and therefore are a key ingredient of reformulated gasoline. At the present time MTBE is practically the only ether produced world-wide. It is formed by the reaction of methanol and isobutylene contained in C4 cuts over an acidic ion exchange resin type catalyst.

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TAME produced from isoamylenes contained in C5 cuts is gaining interest because of its low RVP and because it eliminates photochemically reactive and high RVP isoamylenes.

When ethanol is used instead of methanol; ETBE and TAEE, respectively, are produced from isobutylene and isoamylenes.

2. IFP EXPERIENCE IN OXYGENATES PRODUCTION

To fill the need for new «all purpose» blending components, IFP has developed and successfully commercialized state-of-the-art MTBE, TAME and ETBE Processes. The first MTBE and TAME industrial units were started up, respectively, in 1986 and 1987. Presently, IFP has 10 MTBE Units in operation and 4 under construction, having a combined capacity of 900,000 tons/year of MTBE.

Although MTBE has a leading position in the gasoline pool, further growth of etherification processing will also include TAME. This trend is already confirmed by the commercial success of the IFP TAME process (5 units in operation and 1 under construction).

Finally, ETBE emerges in Europe and specifically in France as the preferred oxygenate provided that ethanol production is subsidized. Anticipating future requirements, IFP has developed a Process to fulfil the forthcoming demands.

Following several industrial production tests, an IFP MTBE unit retrofitted for ETBE production has been in commercial operation for 3 years. Two additional units have been designed with the flexibility to produce ETBE or MTBE. One unit started-up recently while the other one will go on stream during the 4th quarter of 1996. Several other units are in advanced stages of negotiation.

More than 10 years of commercial experience in MTBE using both external reactors and combined reactive distillation systems plus many years of development of our industrially proven TAME and ETBE technologies, have put IFP in the forefront among those actually offering all the processes.

3. CATACOL TECHNOLOGY

IFP has recently developed a new reactive distillation system. This system is named Catacol™. In addition to overcoming equilibrium limitations, Catacol™ minimizes catalyst costs because, contrary to other catalytic distillation systems, Catacol™ does not require proprietary internals or catalyst packaging. Although recently marketed, four applications of Catacol™ will be on-stream for MTBE production in the near future, thereby substantiating the competitiveness of this technology.

Reactive Distillation: Advantages and Disadvantages

Advantages

- **Equilibrium shift**

A number of chemical reactions are limited by the laws of thermodynamics. Operation with excess of one of the reactants shifts conversion towards the desired product of reaction. However, operating in this fashion increases processing cost (recycling of reactant in excess) while not always ensuring complete conversion of the desired reactant.

When the product of the reaction is heavier (or lighter) than the reactants, performing the reaction in a distillation environment enables continuous removal of the reaction product thereby displacing the equilibrium limitation. This holds true in the case of etherification reactions as shown in the following example.

Production of MTBE

$$\mathrm{MeOH} + \mathrm{IC_4} = \Leftrightarrow \mathrm{MTBE}$$

Boiling Point

(1) - 7° C   55° C

(1): Methanol makes a low boiling azeotrop with C_4's.

- **Minimization of equipment**

  Since the reaction is carried-out in the distillation column, a reactor and auxiliary equipment can often be eliminated. This minimizes capital expenditure.

Disadvantages

- **Catalyst replacement**

  Since reaction and distillation take place in the same equipment, catalyst change-out requires stopping the distillation and therefore shutting down the whole plant. However, with conventional systems, using several reactors in series, catalyst replacement or regeneration can be accomplished with the unit still on line. Although conversion is lower during catalyst change-out, the distillation capabilities are still available in a conventional system.

- **Catalytic cost**

  Special packaging or proprietary internals are required to introduce the catalyst in the catalytic distillation. This significantly increases the catalyst cost for the process.

  The combination of high catalyst cost and unit shut-down may tempt operators not to replace the deactivated catalyst in a catalytic tower. The reactive distillation is then operated as a simple distillation and conversion is significantly decreased.

  Installation of guard beds or severe pre-treatment reduces the potential for deactivating the catalyst in the reactive distillation. However, this has a cost and, depending upon the types of contaminants, may not be completely effective.

Catacol™ Objectives and Design

Catacol™ Objectives

1) Take advantage of the equilibrium displacement offered by a reactive distillation system.

2) Minimize catalyst cost and allow easy loading/unloading of the catalyst.

3) Ensure maximum use of the catalyst activity.

4) Maximize distillation efficiency to displace thermodynamic equilibrium.

Catacol™ Design

Catacol™ is a reactive distillation system which overcomes equilibrium limitations and maximizes conversion.

- Minimization of the catalyst cost is achieved by bulk loading of the catalyst. This is made possible by a patented specific design of the reactive distillation internals.

  Bulk loading provides several significant advantages:

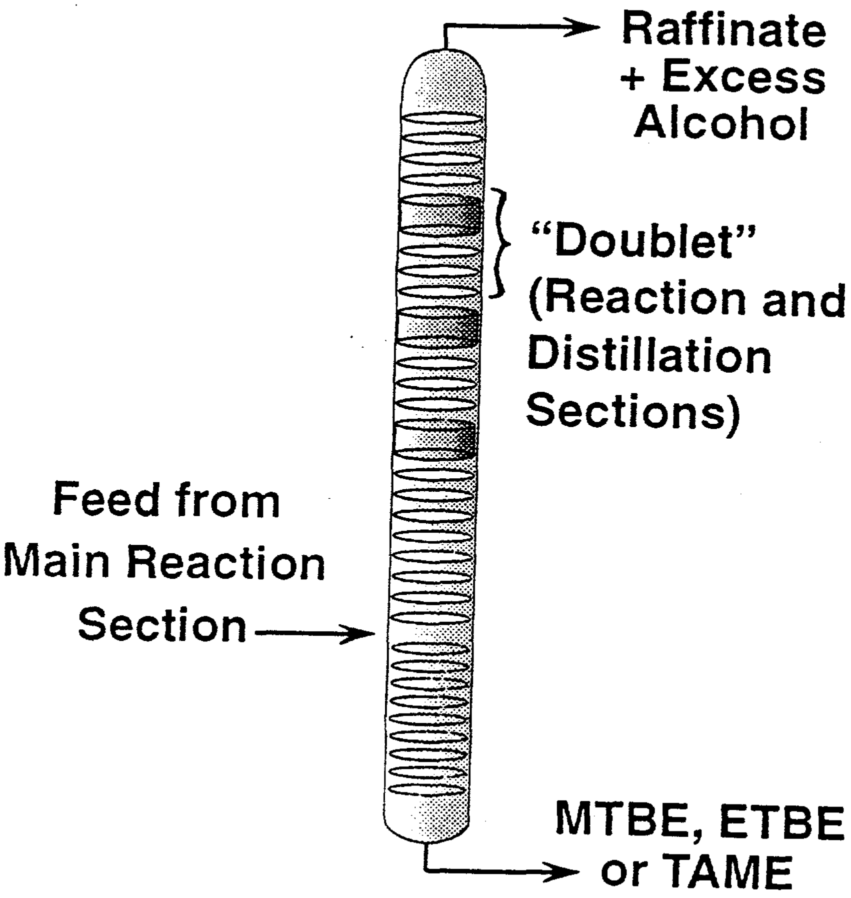
  - since no packaging of the catalyst is required, the overall catalytic cost is reduced,
  - the loading and unloading of the catalyst is much easier to achieve. This minimizes the down-time requirement for catalyst change-out,
  - when unloaded, the catalyst can be easily regenerated without having to separate the catalyst from its packaging.

Catacol reactive distillation system

Although integrated in the same equipment, the distillation and reaction functions are separated in the Catacol™ design. This allows optimization of each function. Catacol™ consists of a series of reaction and distillation modules.

An overall view of the Catacol™ reactive distillation system is shown in figure 1 for etherification applications.

Figure 1 - Catacol™ - «Doublet» Concept



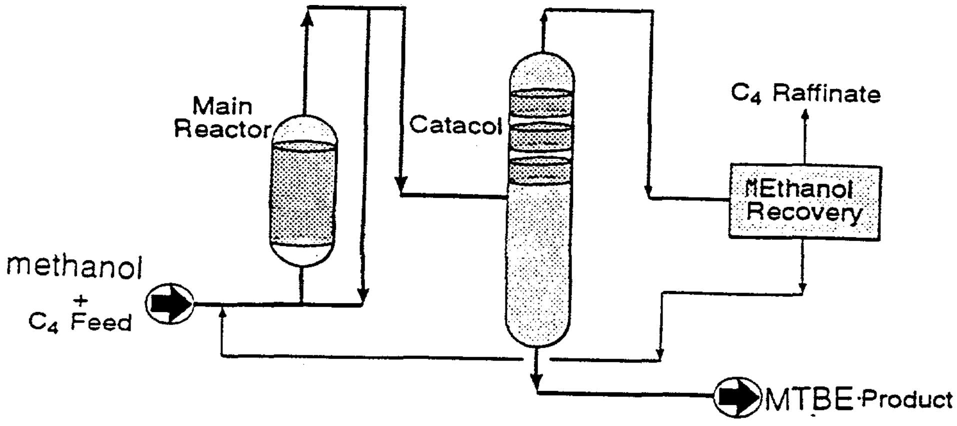
Catacol Internal

The reaction module operates in the liquid phase -upflow- and is filled with bulk loaded catalyst. The catalytic beds are flooded with liquid and the heat of reaction is removed by vaporization. Liquid from the reaction module flows by gravity to the distillation module below. The vapor from the distillation module by passes the reaction module and, together with the vapor from the reaction section, goes to the distillation module above.

Overall process description

Figure 2 shows a processing scheme corresponding to an isobutylene conversion of more than 98%. It includes an expanded bed type front reactor associated with the Catacol™ reactive distillation step as a finishing section.

Figure 2 - MTBE via Reactive Distillation



- **Main reaction section**

Most of the isobutylene conversion occurs in the main reactor which is designed specifically for good thermal and mechanical functioning of the catalyst.

This reactor is operated in the up-flow mode; a liquid recycle ensures the proper expansion of the catalyst bed and removal of the heat of reaction.

The expanded bed reactor offers the following advantages when compared to either a fixed bed reactor or a tubular reactor:

- inexpensive type of construction,
- long catalyst life since no local overheating takes place due to the efficient heat transfer created by the bed expansion between the catalyst grain and the liquid,
- easy loading/unloading,
- high flexibility concerning isobutylene concentration and feed throughput,
- no pressure drop build-up in the catalyst bed.

- **The reactive distillation section**

MTBE and the unconverted C4's are separated in a reactive distillation column which recovers:

- the unconverted C4's and the excess Methanol which forms an azeotrope as distillate,
- the MTBE as bottoms product.

Taking place simultaneously within the column, along with the separation, the finishing conversion step which employs the Catacol™ reactive distillation system placed in the column's upper section consisting of a series of reaction and distillation modules (doublets). The number of doublets determines the overall isobutylene conversion. The combined effect of the Catacol™ system is that the MTBE is distilled away from the reaction zones as soon as it forms. Because the MTBE concentration remains low and because of the presence of excess Methanol, the reaction is driven towards high conversion of isobutylene to MTBE.

4. APPLICATIONS

Debottlenecking of existing MTBE unit

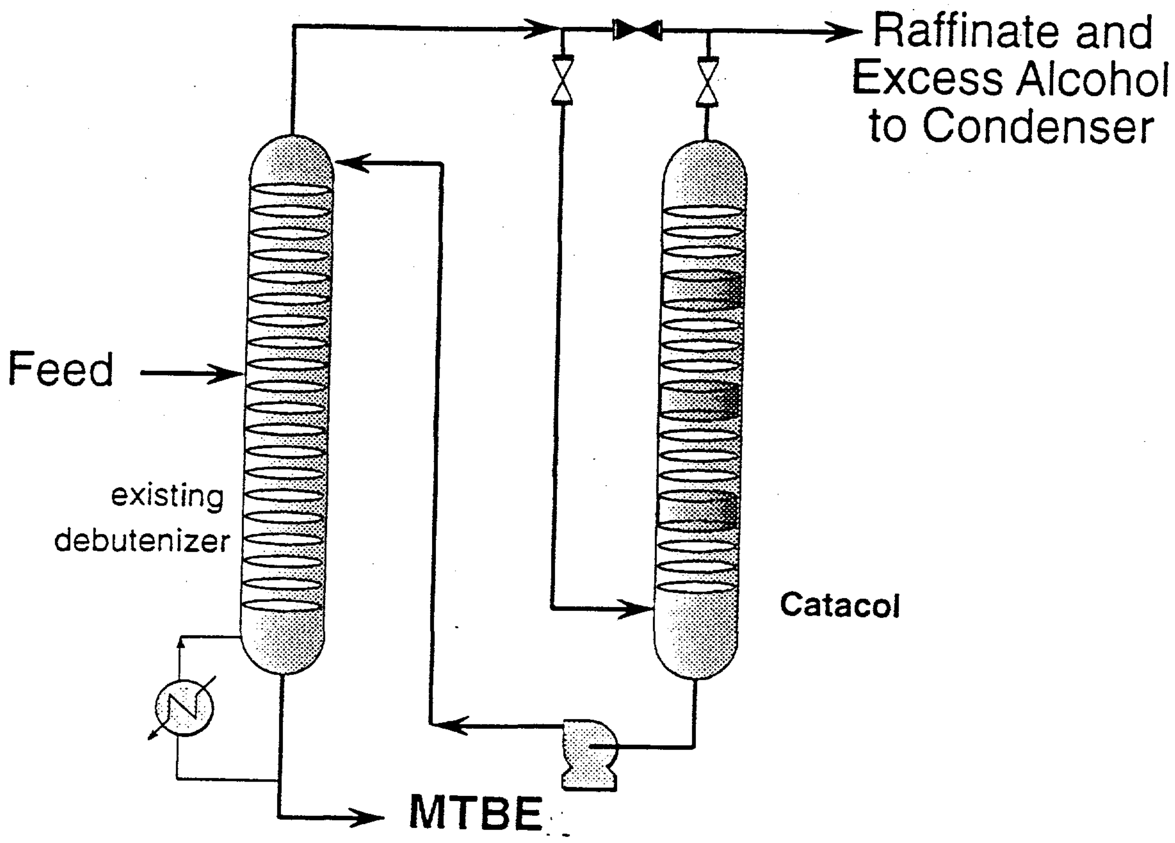
Addition of a Catacol™ section to an existing ether plant is a way to improve conversion when debottlenecking the existing unit.

This add-on requires modest additional investment and provides a very large degree of flexibility of operation. For example, the Catacol™ add-on can be disconnected from the main distillation section for catalyst change-out. Therefore, no unit shut-down is required during this operation.

In this application (figure 4) the Catacol™ reactive distillation section is integrated between the overhead and the condensing system of the existing debutanizer: vapor overhead stream feeding the bottom of the additional Catacol™ column while liquid from the bottom of the Catacol™ column is resent to the debutanizer as internal reflux by means of a transfer pump.

Such a revamp has been selected by an IFP licensee to boost capacity by nearly 50% while improving overall isobutylene conversion and will go on stream during the 4th quarter of 1996.

Figure 3 - Unit Revamp with Catacol™



ETBE production

ETBE is likely to be a key component in the forthcoming premium-grade gasoline pool challenge, due to vapor pressure limitations in reformulated gasoline. ETBE offers excellent blending properties in terms of octane number and vapor pressure:

- lower volatility and higher boiling point offer some key benefits:
  - environmental benefits: it makes a significant contribution in reducing gasoline RVP, which finally reduces VOC emissions (ozone precursors),

  - economic benefits: it allows higher concentrations of butane, even in summer gasoline, improving the economics of RFG blending,

- high octane enables an RFG blender to substitute ETBE for aromatics as a source of RFG octane,

- increased dilution effect: + 15% by comparison with MTBE. For US refiners, this means that a higher clean volume will provide more reduction via dilution in the level of aromatics, olefins and sulfur,

- better Motor Octane Blending Numbers, compared to corresponding MTBE blends, which allows maximum aromatics (including benzene) replacement.

ETBE process

- **Ethanol feedstock**

The renewable alcohol source is agriculture: corn, wheat, sugar cane or sugar beets can be used as starting material to produce ethanol.

The impact of ethanol quality has been extensively investigated to allow for a lower quality raw feedstock. For ETBE manufacturing, the ethanol is supplied under its dry form (0.3 wt % water) but additional rectifications are not required.

- **ETBE processing scheme**

Conventional MTBE unit can be used without modification to produce ETBE, Catacol™ column can also be used leading to higher isobutylene conversion around 95%.

- **Product quality**

Commercial ETBE, wt%

ETBE purity	> 96
Ethanol + TBA	< 3.5
Water	300 ppm max.

Retrofit of MTBE units for ETBE production

The background in the field of oxygenates production, combined with large scale ETBE production experience, allows IFP to provide the expertise for ethanol processing in existing MTBE unit. For example, the impact of ethanol impurities has been investigated to define the cheapest acceptable feedstock and adequate purification. The optimization of the operating conditions, e.g. the ratio ethanol/isobutylene, has been evaluated and checked to maximize ETBE production and purity.

The main questions to be addressed for the retrofit of an MTBE plant to ETBE production are the following:

1) isobutylene conversion required,

2) ethanol quality and pre-treatment,

3) ETBE product quality (Ethanol, TBA, others),

4) C_4 raffinate quality.

All of these questions have been intensively investigated by IFP and checked either at the pilot scale or on industrial units.

5. OTHER APPLICATIONS OF CATACOL™

- Besides etherification, Catacol™ can be employed for a number of applications. Catacol™ can be used not only for equilibrium limited reactions but also to displace azeotropes. This is the case of Benfree™, another application of Catacol™, especially useful when light reformate isomerization is envisioned.

Benfree™ significantly improves the economics of processing a light reformate in a paraffin isomerization unit. Benfree™ utilizes commercially proven catalyst to saturate benzene into cyclohexane in the reformate splitter using Catacol™ technology. Since cyclohexane does not form a low boiling azeotropes with C7's, Benfree™ produces a benzene and C7 free feed to the isomerization unit. In addition, Benfree™ can be designed to drop cyclohexane with the heavy reformate and produce a relatively naphthene free feed to the isomerization unit. The distillate from the reformate splitter then becomes a very easy feed to isomerize and mild operating conditions can be used in the paraffin isomerization unit.

CONCLUSION

IFP enjoys a privileged position in the field of etherification for the following reasons:

- it is a Licensor for all the major etherification processes: MTBE, TAME and ETBE,

- it has the capability to tailor the Process to the customers specific needs,

- it has acquired vast industrial experience in ETBE manufacture through large scale and long term commercial operations.

Moreover, IFP offers a new type of reactive distillation under the trademark of Catacol™. The Catacol™ design alleviates the drawbacks of existing catalytic distillation systems (high catalyst cost) while achieving high conversion. Catacol™ can be applied to grassroot etherification units or to revamp existing plants. It can also be used to convert MTBE units to ETBE manufacture.

Catacol™ can be applied to a number of other applications such as Benfree™ which employs the Catacol™ technology to hydrogenate benzene in a reformate splitter and produce a C7 and naphtene free feed to a paraffin isomerization unit. This will be the topic of future presentations.