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Light olefins dimerization to high quality gasoline components

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Abstract

New attractive technologies can be designed in the field of light olefins dimerization (C_3–C_5) in order to obtain products useful as gasoline blending components; the technologies are characterized both by low investment costs and by high product quality. Isobutene dimerization is a powerful alternative to MTBE production whenever the use of the latter will be forbidden in gasoline. Also the dimerization of iso-amylenes and propylene, when properly designed, can give products (both the olefins and the corresponding hydrogenated derivatives) characterized by very high octane numbers. More in general all these technologies can help to debottleneck the FCC downstream when enhanced olefins production is achieved by means of new FCC catalysts and processes.

Keywords: Olefins dimerization; Isooctane; Alkylate; Propylene; Isobutene; Isoamylenes; Acid catalysis; Nickel complexes

1. Introduction

Gasoline reformulation is undoubtedly a worldwide trend [1]. Phase II of the complex model of the US Clean Air Act Amendment is now in force to fuel US cars with more environmentally friendly gasoline. In Europe a new legislation for the year 2000 (and partially also for 2005) has been issued [2]. Other countries, including Mexico, Japan and China, are on the way to promulgate new regulations concerning gasoline properties.

The worldwide guidelines in this field are the reduction of evaporative emissions and a more complete gasoline combustion. To this purpose, oxygenates and highly branched paraffins, such as those present in alkylate, will play a major role as gasoline components, together with a general reduction in volatility (RVP), aromatics, olefins and sulphur content.

However, the mostly used oxygenated compound, methyl-*tert*-butyl-ether (MTBE), is in jeopardy; as the effect of the state ground waters contamination, on March 1999 the Governor of California decided the ban of MTBE from gasoline since the beginning of 2003. This resolution will cause the phase out of about four MPTY of ether from US gasoline. Also the US EPA is ready to favour a reduction of the MTBE content in the rest of the US reformulated gasoline [3].

Taking into account all these aspects, branched saturated hydrocarbons represent a very important class of compounds for gasoline reformulation; they can be achieved in different ways in the refinery: either by isobutane alkylation with olefins, either by C_5–C_6 *n*-paraffins (skeletal) isomerization (but octane number lower than 88) or by light olefins dimerization (also called polymerization when referred to the refinery field).

Alkylate is particularly suitable for its high octane number (90–96), the low volatility (3–5 psi) and the absence of sulphur and aromatics. Alkylation is a

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well-established process; however, a number of environmental concerns will cause increasing troubles for new plants based on the present technologies: hydrofluoric acid should be ruled out for installations in populated areas due to its extreme toxicity, while sulphuric acid is highly corrosive and produces huge amounts of acid muds difficult to dispose. Alternative processes with solid acid catalysts are being developed but their commercial applicability has still to be proved [4].

As regards dimerization/polymerization, it is well-known that propylene and butenes can be oligomerized (polymerized) to form a high octane product boiling in the gasoline range [5]. The product is olefinic and has unleaded octane numbers of 97 RON and 83 MON. The polymerization process was widely used in the 1930s and in the 1940s to convert low boiling olefins into gasoline blending stocks but was supplanted by alkylation after World War II. However, the mandated reduction in use of lead in gasoline and the increasing proportion of the market demand for unleaded gasolines has created a need for low-cost processes able to produce high octane gasoline blending components.

Typical dimerization (polymerization) catalysts are acid ones, the most widely used being phosphoric acid on an inert support. Typical olefins processed are butenes (generally containing relevant percentages of isobutene) and propylene. Isobutene dimerization may be carried out in the liquid-phase with acid catalysts, the main problem is to control the reaction temperature to prevent producing large amounts of compounds beyond the dimers, i.e. oligomers (about 20–25% of trimers and more than 2% of tetramers) [6]. Tetramers fall outside the gasoline boiling range and, as regards trimers, such a high percentage of high boiling compounds is not acceptable in “Cleaner Burning Gasolines”. Propylene gives mostly trimers (C_9) with only 10% conversion to dimers (C_6).

The polymerization reaction is highly exothermic and the temperature is controlled either by injecting a cold propane quench or by generating steam. The propane and the butane in the feed act as diluents and as heat sink to control the rate of reaction and the rate of heat release. Gasoline boiling range polymer is normally 90–97% on olefin feed (depending on the olefin used) or about 0.7 barrel of polymer per barrel of olefin feed.

Institut Francaise du Petrole (IFP) has also developed a different process (Dimersol-G) to produce Dimate (Isohexene) from propylene using a homogeneous nickel–phosphine catalyst promoted by aluminium alkyls (both not recoverable). The major advantage of this process with respect to the previous one is the low capital cost because it operates at low temperatures and therefore at low pressure [7].

Thus, dimerization/polymerization could be a flexible and relatively low-cost process for converting low value LPG or light olefins produced by FCC to higher value gasoline; however, the new more stringent regulations on gasoline formulation require in addition a few problems to be overcome:

- if necessary, olefins have to be converted to isoparaffins, preserving excellent octane properties;
- more stringent regulations on distillation curve have to be met: thus high amounts of heavy compound are no more justifiable.

In this framework, a systematic study on the selective dimerization of C_3–C_5 olefins has been performed.

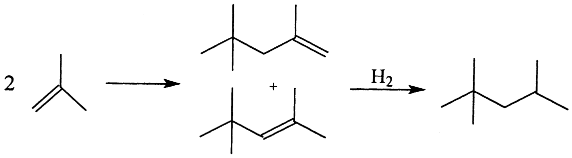
2. C_4 cut — isobutene dimerization

At first, we decided to maximize the flexibility of Snamprogetti etherification technologies by making it possible to produce a high quality alkylate if and when needed or convenient, as well as continuing to produce some MTBE (or ETBE) as needed [8].

Carrying out the MTBE synthesis under sub-stoichiometric conditions, i.e. MeOH/isobutene 0.2–0.6 mol/mol, it is possible to produce simultaneously and in a wide range of relative ratios MTBE and isobutene dimers, namely 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene [9].

As the hydrogenation of isobutene dimers yields isooctane (2,2,4-trimethyl-pentane), which is both the main component of the alkylate and the reference compound for rating the gasoline octane properties ($\mathrm{RON} = 100,\ \mathrm{MON} = 100$), 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 [10].

This process is called Isoether DEP (dimerization/etherification process), and produces simultaneously an isooctane-based high quality alkylate (called Iso-OctAne) and MTBE (or ETBE). The process consists of two reaction stages: first, in a water cooled tubular reactor, isobutene is partially etherified into MTBE and partially oligomerized into a di-isobutenes rich fraction (called Iso-OctEne); in a second stage, the latter fraction is hydrogenated to Iso-OctAne.



The key point compared to other dimerization processes is the possibility of removing the reaction heat as soon as it is released along the bed length: both the reactions are exothermic ($\Delta H_{\mathrm{Ether}} = -9.5\,\mathrm{kcal/mol}$, $\Delta H_{\mathrm{Dimer}} = -19.8\,\mathrm{kcal/mol}$) and a poor control of temperature profile inside the reactor leads to losses in selectivity. For this reason, the Isoether process is carried out in the presence of alcohol (see hereinafter in the text) and in a water cooled tubular reactor, where the reaction heat is removed as soon as it is generated along the catalyst bed length. Under optimal conditions the formation of trimers is limited to <10 wt.% in Iso-OctAne, tetramers are present at levels of thousands of ppm. The alcohol nature and the C_4 source influence the overall selectivity and the quality of the product.

2.1. Effect of the alcohol

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 according to the following reaction:

$$SO_3{}^-H^+ + MeOH \rightleftarrows SO_3{}^-MeOH_2{}^+ \tag{1}$$

Since $MeOH_2{}^+$ is a less acid species than H^+, the rate of the oligomerization reactions is much reduced; this positively affects the selectivity to dimers. Further, 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.

This effect is not only typical of methanol but also of higher alcohols; very attractive results have been achieved also with ethanol and iso-propanol [11], both the alcohols further reducing the formation of trimers; furthermore, the corresponding ethers (ETBE and IPTBE) have high octane and are attractive when their use in gasoline is allowed.

When tertiary alcohols, such as *tert*-butanol, are employed, no ether is formed due to steric hindrance and pure dimerization is achieved [12]. Pure dimerization can be achieved also by using ethers (such as MTBE, ETBE, etc.) as catalyst acidity moderators.

By employing these concepts Isoether 100, a modification of Isoether DEP, has been developed in order to expand the ratio of the achievable Iso-OctAne/ether simultaneous productions beyond the Isoether DEP limits till to the extreme extent of producing only the hydrocarbon product without ether occurs. This avoids the simultaneous MTBE production whenever ether production is undesirable or unfeasible.

2.2. Effect of the C_4 feedstock source

The dimerization process makes use of any C_4 feedstock coming from any available source (steam cracking, after butadiene removal, fluid catalytic cracking, isobutane dehydrogenation, from *tert*-butanol dehydration). Depending on the feedstock composition, the Iso-OctAne product quality will be different. The C_4 feedstocks differ, in fact, due to their isobutene content, content of normal butenes and to the split between 1-butene and 2-butenes.

In MTBE synthesis, *n*-butenes are practically inert. In dimerization, instead, *n*-butenes can react to a low extent (5–10%) with isobutene, making C_8 co-dimers, which after hydrogenation are transformed into isooctane isomers [9]. The clear octane numbers, obtained depending on the C_4 distribution in the feed, range from $\sim$97 to $\sim$100. In Table 1 the main characteristics of Iso-OctAne and of the parent olefin product, Iso-OctEne, are reported.

Iso-OctAne quality is better than that of normal alkylate, since its octane properties are improved and its volatility is lower. Furthermore, its production is "environmentally friendly" because the hazards coming from handling hydrofluoric acid or sulphuric acid in alkylation processes are completely removed; the ASTM distillation curve of Iso-OctAne and that of

Table 1
Iso-OctAne and Iso-OctEne properties vs. alkylate and MTBE

Feedstock source	Iso-OctAne		Iso-OctEne		Alkylate	MTBE
	Dehydrogenation	FCC	Dehydrogenation	FCC		
Clear RON	100.2	99.4			96.0	
Clear MON	100.3	98.3			94.0	
Blending RON	101–103	100–102	114–118	112–115	97–99	116
Blending MON	96–98	94–97	95–97	93–96	90–92	100
RVP (psi)	1.7	1.7	1.5	1.6	4.5	8.0
Specific gravity	0.720	0.702	0.733	0.728	0.697	0.745

normal alkylate overlap in the heavy part but not in the light one reflecting the difference in RVP. Also the parent olefinic product (Iso-OctEne) has very high octane numbers (blending RON ca. 113–117 and blending MON of 93–96) and has a very low vapour pressure. In those areas where the legislative limitations to the olefins content in gasoline are not stringent, Iso-OctEne can be blended directly into the gasoline pool or sold on the marketplace as a high octane and low RVP hydrocarbons component.

2.3. Effect of the catalyst

As regards the effect of the nature of the catalyst, different ionic resins have been tested under Isoether DEP conditions; both the acid concentration and the distribution of the acid sites between bulk and surface were varied.

It was observed that the most active catalyst is the most acidic, i.e. Amberlyst 35 (as shown in Fig. 1): no or small difference was observed as regards the conversion to MTBE but the conversion to oligomers was clearly influenced by the concentration of acid sites.

As regards the selectivity to dimers some influence was observed in the resins with the acid sites mostly located on the surface disfavouring higher oligomers formation.

3. C_5 cut — iso-amylenes dimerization

Also the iso-amylenes dimerization technology could be attractive because it might concur to reduce the light olefins concentration as these olefins are undesired atmospheric ozone precursors.

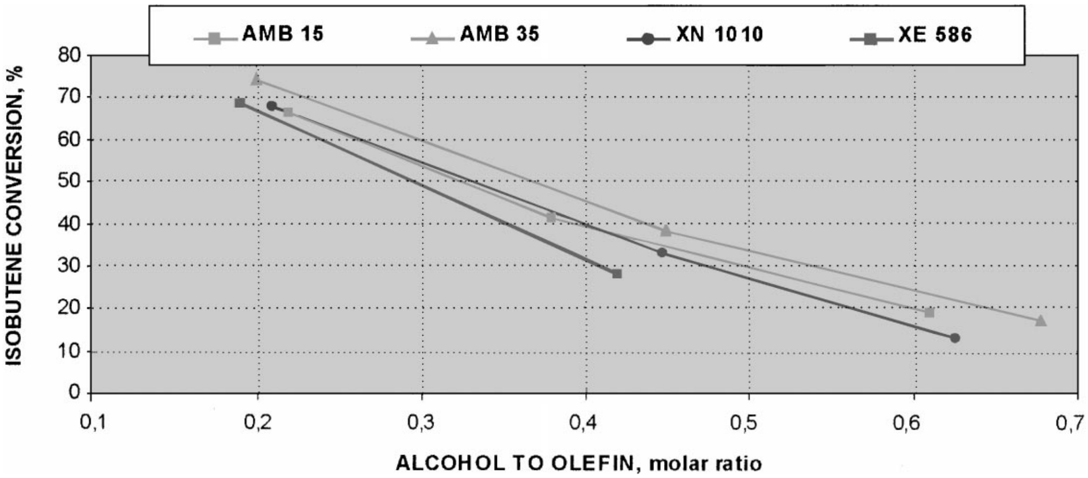


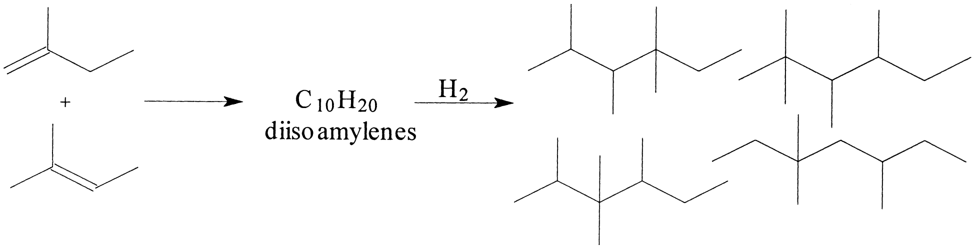
Fig. 1. Isobutene dimerization in the presence of cationic resins (T ca. 50°C, LHSV $= 7\,\mathrm{h}^{-1}$).

Table 2
Physical properties of the acidic resins employed[a]

	Acid sites distribution	Concentration of acid sites (meq H^+/g)	Surface area (m^2/g)	Pore diameter (nm)
Amberlyst 35	Surface/bulk	5.2	44	20
Amberlyst 15	Surface/bulk	4.8	45	24
Amberlyst XN1010	Mainly surface	3.3	570	5
Amberlyst XE586	Only surface	1.3	50	25

[a] All furnished by Rohm and Haas.

The reaction has been investigated and the following observations are worth to be reported.



Resin catalysts (the same reported in Table 2) are very active, the best ones being those with the acid sites mostly located on the surface (Fig. 2); in this case, in fact, cracking and further oligomerization reactions are minimized.

Under optimal conditions the selectivity to dimers (C_{10}) is higher than 92–93% with trimers (C_{15}) formation lower than 8%.

In the presence of methanol (also when present in trace concentrations), no oligomers were produced, TAME being the only product observed. In this case the reaction is slower with respect to isobutene dimerization and catalyst acidity has not to be partially moderated.

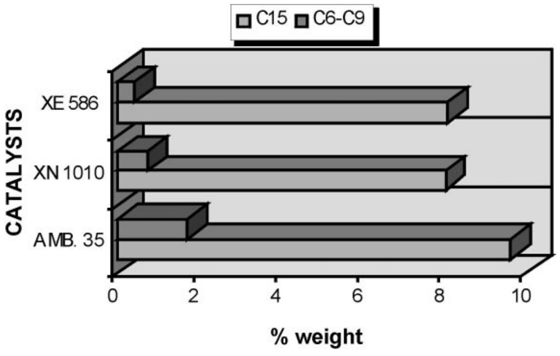


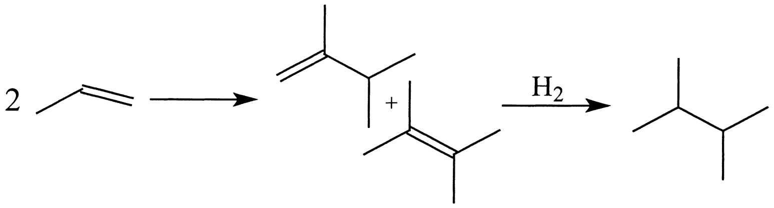
Fig. 2. Isoamylenes dimerization in the presence of cationic resins ($T = 60$°C, LHSV $= 4\,h^{-1}$).

The product when hydrogenated displays a very high octane number (blending RON: 105, blending MON: 85); RVP is very low (<0.5 psi), however the product is very high boiling with 95% of the product boiling at temperatures higher than 145°C.

4. C_3 cut — propylene dimerization

Dimersol-G process has a lot of advantages but, if the olefin product has to be hydrogenated, the octane quality rapidly falls from 97 to ca. 82 for RON and from 82 to 78 for MON.

In this case an improved process should be developed for the conversion of propylene to high quality gasoline: the catalytic selective propylene dimerization to 2,3-di-methylbutenes (2,3-DMB) appears suitable for obtaining, after hydrogenation, high octane number gasoline blending components. In fact, the hydrogenated derivative, 2,3-dimethylbutane, displays an RON of 104 and an MON of 94.



Thus, if selectivities to 2,3-DMB higher than 80–85% are reached, octane quality can be preserved after hydrogenation. A preliminary study was accomplished by studying the catalytic performances of (β-dithioacetylacetonate)(phosphino)nickel(II) complexes in terms of regioselectivity and productivity of 2,3-DMB [13]: it was observed that the most suitable ancillary phosphine ligand must be characterized by high basicity and at the same time by a relevant bulkiness, such as that of PCy_3 and P^iPr_3.

When a phosphine ligand of the above characteristics was adopted, the major role is played by the nature of the organoaluminium co-catalyst. Indeed, both activity and regioselectivity of the process are influenced by the Lewis acidity of the co-catalyst. In this respect, a certain acidity appears necessary for the activation of the nickel precursor, but on the other hand, too high acidity such as that of $EtAlCl_2$ favours the formation of higher and less branched oligomers. Therefore, an intermediate acidity could be ideal to promote the catalytic system in order to achieve optimal activity and selectivity to 2,3-DMB.

For example, the use of the $Et_3Al_2Cl_3$/(β-dithioacetylacetonate)(phosphino)nickel(II) system and that of the same complex with mixtures of Et_2AlCl and methyl-alumoxane (MAO) resulted attractive to modulate the selectivity of the oligomerization process by achieving selectivity to 2,3-DMB in the C_6 fraction till 84% and containing the production of higher oligomers (mainly trimers) below 20%. A detailed analysis of the composition of trimeric products was also performed in order to gain important informations on their octane characteristics as well as on mechanistic implications [13].

Following the latter principles, another new nickel-based homogeneous catalytic system has been developed by us [14]; the catalyst, promoted by bulky phosphines and intermediate acidity chloro-alkyl alumino compounds, is very active (operating at $T = 0$–$5°C$) with selectivity to 2,3-DMB in the C_6 fraction till 85–90% and with the formation of higher oligomers confined at levels lower than 20%.

After hydrogenation, the overall product has blending RON of 95–99 and blending MON of 86–90; the product displays properties sharply improved with respect to that from Dimersol-G (olefin product with 97 RON and 82 MON) and to that from propylene alkylation (saturated product with 90–93 RON and 89–91 MON) [5].

5. Conclusions

In this work we have shown that new attractive technologies can be designed in the field of light olefins dimerization (C_3–C_5); they are characterized both by lower investment costs and by higher product quality.

The isobutene dimerization technology is a powerful alternative to the use of isobutene when MTBE use in gasoline will be forbidden. It is worth noting that the Isoether technology has been extensively tested in an industrially homologous pilot plant. A first commercial Iso-OctEne and MTBE combined production was carried out in 1997 in the industrial Ecofuel MTBE plant at Ravenna, Italy. Many industrial production tests have been carried out starting from 1997 in several plants worldwide and many thousands t of products have been produced.

More in general, all these technologies can help to debottleneck the FCC downstream when enhanced olefins production is achieved by means of the new FCC catalysts and processes [15]. In fact, this kind of solution leads to an increased production of light olefins (C_3–C_5) and also modifies the internal composition of the C_4 and C_5 cut. For example, olefins production is increased with respect to paraffins and also branched olefins are increased with respect to linear ones.

This is a remarkable result which, however, involves a heavy economical burden since the whole

FCC downstream will need to be accordingly revamped. However, improved light olefins dimerization technologies could represent cost-effective and flexible solutions to transform the C_3–C_5 light olefins into high quality products and to accomplish at the best the future regulations on gasoline formulations.

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