Recent progress in refinery alkylation: Premium octane blends from safer catalytic processes

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Abstract: Refinery alkylation is becoming the major source of high-octane gasoline blends. Processes based on liquid mineral acid catalysts may in time be replaced by novel processes employing new alkylation technologies that use ionic liquid acids and solid acids as catalysts. Market penetration is already under way. Additionally, future refinery alkylation will involve extension of the types of isoalkane and alkene feeds, to afford higher alkylation capacity by not relying only on isobutane–butene feed streams. New light is shed here on novel refinery alkylation processes and their catalysis, with emphasis on current and future trends of this type of technology.
Keywords: refinery, alkylation, octane.

1. Introduction

The major refinery processes for producing gasoline octane blends are naphtha reforming, isomerization of $C_4 - C_6$ alkanes, and alkylation of isobutane with olefins (mostly butenes). Octane additive processes utilizing solid catalysts are compared in Table 1. In recent years, refinery alkylation producing $C_7 - C_9$ polybranched alkanes (Scheme 1) has been gaining considerable attention and interest.[1] With average annual gasoline production increase of ~1.5% in the U.S., and a parallel increased demand for higher octane blends, alkylation seems to be the only option for expanding production of premium-octane gasoline additives. This is because due to the more stringent regulations against aromatics in gasoline, naphtha reforming is becoming more limited as a fuel source, and is instead geared now more toward producing aromatics for sale and hydrogen for refinery needs. Isomerization has limited use for octane blending since it produces blends of lower octane (Table 1), which are also too volatile (having two-digit RVP). Oxygenates in gasoline are limited by the 2.7% mass oxygen cap, and if solely based on ethanol (as is effectively in the U.S.), they increase gasoline RVP, so their maximal content in gasoline, as octane blend, is further limited. In contrast with all the above, alkylates are "perfect" gasoline octane blends: They contain highly branched polymethyl-alkanes of supreme combustibility, whose octane rating is very high (e.g., >95 RON) and whose RVP is very low (low single-digit), and they are free of contaminants such as aromatics, olefins, sulfur, nitrogen, metals, etc. There is, therefore, a strong impetus in refineries to increase the share of alkylates in gasoline octane blends, and at the same time improve the fuel quality of alkylate blends.

Table 1. Refinery high-octane hydrocarbon production over solid catalysts.

Process	Reaction conditions	Catalyst (typical)	Octane (RON)
reforming	endothermic, ~510 °C	$Pt(Re,Sn)-Cl/Al_2O_3$	80 – 92
isomerization	energy-neutral, 90 – 250 °C	$Pt-Cl/Al_2O_3$, Pt-SZ, Pt-HZSM-5	70 – 85 (>90 with recycle)
alkylation	exothermic, 50 – 100 °C	Pt-HY	90 – 98

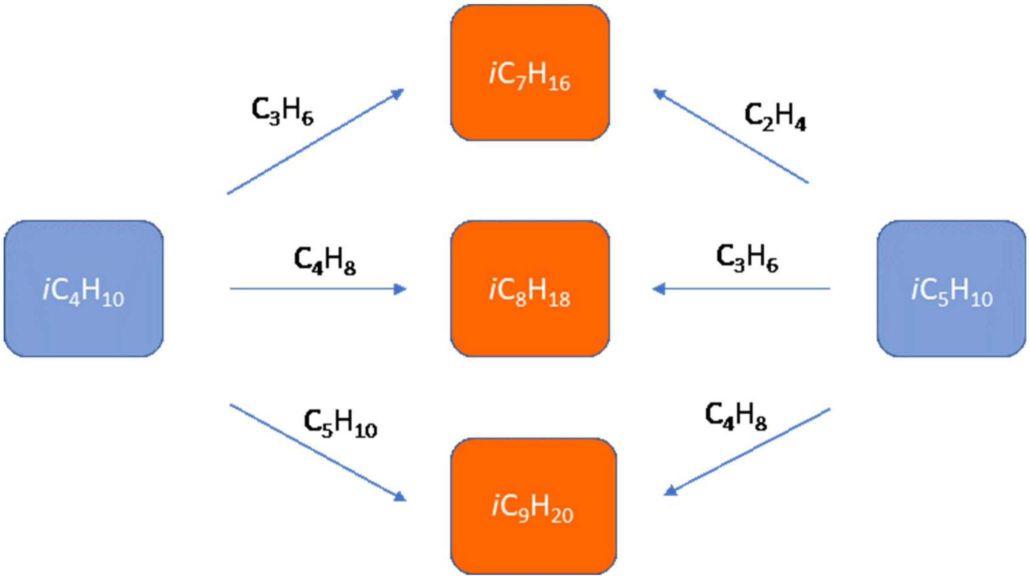
2. Existing refinery alkylation technologies

Traditionally, alkylation in the refinery has involved only liquid acid catalytic processes, and those processes have been based on either sulfuric acid (SA) or hydrofluoric (HF) acid.[1] HF processes first dominated the alkylate market, but later have gradually lost market share to SA processes. This was the result of increasing concerns over safety in unit operation and the consequent mounting of new, more stringent governmental regulations relating to HF emissions and their monitoring and prevention. Risks to the public and the environment are associated also with SA alkylation, but to a lesser extent. HF plants are not being built in the U.S. anymore and phasing out of all existing plants may occur within the next twenty years or so. Over somewhat longer period, SA plants may also be replaced by alkylation units based on better and safer technologies, whether newly built or being retrofitted SA units. Progress in refinery alkylation is now happening in both improved and more economical process engineering and technology, and the introduction of novel catalysts that replace the liquid mineral acids, thus affording safe, risk-free operation.

3. Recent improvements in alkylation technology and catalysis

The purpose of this presentation is to address and critically discuss the newest technological advancements in refinery alkylation, emerging catalytic alkylation processes, and novel catalyst materials of improved performance. An emphasis in made on new industrially-proven alkylation catalysts, such as ionic liquid acids[2] and solid acids based on zeolite molecular sieves,[3] with an in-depth consideration of the details of the structures of those catalysts, and how the structural details influence catalyst's activity, selectivity and durability. In another segment of the presentation, the scope of isoalkane–alkene alkylation is highlighted in terms of its molecular chemistry. This scope is now being extended to include more refinery low-molecular hydrocarbon streams, such as coker gas and oil cracking gas (e.g., FCC off gas). By also using isopentane, ethylene and propylene as reactants (Scheme 1), emerging new alkylation processes will solve the pressing problem refiners now have – accumulating and storing considerable amounts of those byproducts that currently have no effective, value-added utilization. However, for those new alkylation processes to be commercially competitive, refiners may have to operate alkylation units with novel, next-generation superacidic catalysts.

Some ideas for more advanced catalysts are also presented and discussed. Thus, for example, ionic liquid acids may in the future be anchored to solid supports, hence becoming immobilized; this will afford better reactant–catalyst mixing and easier product–catalyst separation, and the possibility of fixed-bed operation. Next-generation solid-acid alkylation catalysts (e.g., those based on zeolites) may incorporate nanocrystallinity and mesoporosity for improved performance and longer durability. Solid-acid processes may have higher catalyst rejuvenation efficiency through employing continuous or semi-continuous modes of catalyst refreshment.



Scheme 1. Major primary isoalkane–alkene reactions in refinery alkylation processes.

4. Conclusions

Refinery alkylation is currently undergoing considerable modernization in its engineering and catalysis technologies. In addition to the desire to replace liquid-acid based processes, current efforts are aimed at increasing alkylation capacity and boosting the fuel quality of the alkylate product. A special attention is given to developing advanced catalytic systems for producing supreme alkylates as gasoline additives of highest octane rating, supreme fuel combustibility, and low RVP.

References

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