Marko Mužic, Katica Sertić Bionda, Tamara Adžamić

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THE OPPORTUNITIES FOR REFINERY PRODUCTION OF ENVIRONMENTALLY FRIENDLY HYDROCARBON FUELS - HYDROCRACKING, ALKYLATION AND ISOMERIZATION

Abstract

Oil industry is faced with increasing pressure, from government agencies and public alike, to improve refinery processes. The main objective of development is to reduce negative impacts on the environment while maintaining economic viability of the entire process. The environmental aspect can be divided into two main parts including the primary task to reduce the plant emissions and secondary task to at the same time produce environmentally friendly hydrocarbon fuels whose improved properties are reflected in reduced emissions from internal combustion engines. The basic refinery processes that are able to produce environmentally friendly hydrocarbon fuels or the so called clean fuels include hydrocracking, alkylation and isomerization. Advances in research and development of new technologies and catalysts increased the value of the aforementioned processes because the environmental risks are reduced and the fuels they produce have high octane/cetane numbers and low or now sulfur and aromatic content depending on the type of feedstock. The alkylation is also researched as possible alternative treatment process for lowering the total sulfur content in gasoline fuels during which there would be no octane loss in the product.

1. Introduction

Total consumption of liquid hydrocarbon fuels at the global level for the period from 2003 and 2010 rose, insight of a slight drop that was recorded in 2007 and 2008 due to the economic crisis. It is estimated that the consumption will continue to rise which will cause a steady rise in production volume of petroleum refining industry.[1,2] The International Energy Agency (IEA) in its World Energy Outlook 2008 estimates that total consumption of petroleum products per annum will rise by 1,3 % until 2020 and by 1,0% from 2020 to 2030 which is in accordance with the published estimates by the U.S. Energy Information Administration (EIA) in its 2010 Short-Term Energy Outlook por the period from 2015 to 2035.[2,3]

The facts that refinery units are consuming between 4 and 9% of the crude they are processing and that liquid hydrocarbon fuels for internal combustion engines make up 80 to 85% of all the refinery products means that the increasing total fuel consumption and their production will cause increase in emissions from both of these sources.[4,5] It has been determined that all modes of transport are producing more then 20% of the total global amount of green house gases.[6] That is why, for many years already, there are environmental protection laws in place limiting refinery emissions as well as the fuel content of compounds which have negative effects on the environment.[7,8] The increase in consumption of liquid hydrocarbon fuel production and refinery capacity in the past lead to more stringent legislation and will continue to do so in the future.

The petroleum refining industry must therefore continuously work on improving and advancing refinery separation, conversion and treatment processes in order to lower the emissions and produce environmentally friendly fuels.

This work gives an overview of recent research results and developments of hydrocracking, alkylation and isomerization processes as conversion technologies for production of environmentally friendly, the so called clean fuels.

The processes of hydrocracking, alkylation and isomerization are generally considered as a group of classic refinery processes but the advancement in the research and development of new catalysts raised their level of importance and value. The new technologies represent lower risk to the environment and can produce gasoline fuels with high octane number and low content of aromatic and sulfur compounds, depending on the feedstock.[9-14] The alkylation is also researched as possible alternative treatment process for lowering the total sulfur content in gasoline fuels during which there would be no octane loss in the product.[15,16]

2. Review section

2.1 Hydrocracking

The growing demand for middle distillates and the increasing production of heavy crude oils have placed hydrocracking as one of the most important secondary petroleum refinery processes. Hydrocracking is commonly practiced in the petroleum refining industry to treat oil residua. During hydrocracking, large compounds are broken to form low molecular weight compounds. When the reaction takes place over a catalyst in a hydrogen-rich atmosphere, other reactions, such as hydrodesulfurization, hydrodemetallization, etc., occur simultaneously.[17] Hydrocracking combines the processes of catalytic cracking and hydrogenation and in order to enable the processing a complex catalyst system must be used. That is why bifunctional catalysts were developed which can simultaneously catalyze hydrocarbon cracking, isomerization and hydrogenation reactions. The best known catalytic systems are synthetic zeolites with metal oxides or sulfides including very efficient Co-Mo and Ni-Mo oxides and Ni-W sulfides.[18]

The recently conducted research in hydrocracking can be divided into two main groups depending on the type of feedstock used. The research is being conducted using the usual heavy oil fractions for testing new catalyst formulations and/or reactor systems and the other research is being conducted using heavy hydrocarbon liquids of the plant origins. The research of the new catalysts for the hydrocracking of heavy oil fractions are primarily focused on the application possibilities of new or modified conventional catalyst supports which control the cracking reactions and must have acid properties. Hydrogenation catalytic components which are metals Co, Mo, Ni i W are well known and the modification possibilities are limited.

The key parameter for the selection and the preparation of the catalyst support is its acidity. High acidity tends to cause coking, which leads to deactivation. In order to prepare a suitable hydrocracking catalyst, a good balance between the two functions has to be maintained. The selection of a proper catalyst for a given high activity is a complex problem. While microporous zeolites such as Y, ZSM-5 and β are playing important roles in modern petrochemical industry for their abundant uniform microporous structures and strong intrinsic acidities, much attention is being given to the development of mesoporous zeolites that provide larger pores (N2 nm) to allow the conversion of large molecules and thus overcome the limitations of microporous zeolites. At present, a popular solution is to prepare a composite zeolites material comprising of both the microporous zeolites matrix and mesoporous material by multi-step crystallization.

However, all of these methods mainly aim at modifying mesoporous material on its structure stability and acidity, whose level of standard are still far away from microporous zeolites. One of these mesoporous zeolites that have aroused many research interests is the so called MCM-41. Despite the intensive research on synthesis, characterization and application of MCM-41 materials, MCM-48, being the cubic member of the M41S family, has received much less attention especially in the field of catalysis.[19]

Rana et. al[20] studied a bifunctional catalyst with active CoMo metallic sites and composite meso and macro-porous support prepared by the mixing of alumina and ultra-stable Y zeolite (US-Y). Fig. 1 shows the results of catalytic activity of the CoMo catalyst at micro-flow evaluation scale using heavy oil. Hydrodseulfurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM) and hydrogenation of asphaltenes (HDA) conversions are presented as a function of time-on-stream at different temperatures. The catalytic results indicate that the catalyst is more active for hydrogenolysis (HDM, HDS, HDN) than hydrogenation (HDAs) function, which could be due to the CoMo active metal, and that the catalyst activitiy is increased with the rise in temperature. However, at 420 °C high pressure drops occured in the reactor due to the excess of cracking; whose gaseous hydrocarbon paraffins (C1–C3) may precipitate asphaltenes or form sediments at high temperature.

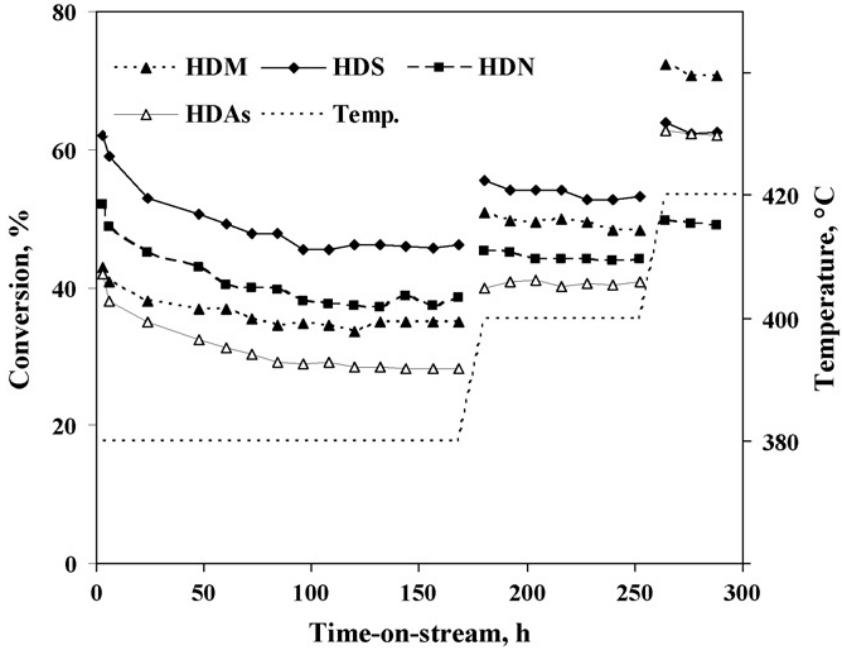

Figure 1: Catalytic activities of supported CoMo/γ-Al_2O_3-US-Y zeolite with time-on-stream at different temperatures [20]

Additionally it was determined that the bi-modal type of pore in the catalyst contributed to the combination of hydrodesulfurization (HDS), hydrodemetallization (HDM) and the selective hydrocracking of asphaltenes over the acidic catalyst. An increase in temperature specifies that HDM and HDAs reaction rates are faster than HDS and HDN ones, thus, the results sustain a thermal cracking of complex molecules like asphaltene and metal porphyrins, which is also confirmed by the gaseous product selectivity of the hydrocarbon.[20]

Shimada et al.[21] studied the new NiMo sulfide catalysts with MTZ Y zeolite-based supports they designed and developed for hydrocracking heavy petroleum. The supports consisted of modified ultra-stable-Y zeolite (MTZ) and an Al_2O_3 binder. The MTZ was prepared by immersing ultra stable-Y zeolite in aqueous $Ti(SO_4)_2$ solutions, followed by Mo loading with the equilibrium adsorption of ammonium heptamolybdate.

Fig. 2 shows an example of the catalytic activity tests in a continuous flow-type reactor with a fixed catalyst bed. The midle disttilate, gas and naphtha yields increased over time at temperatures of 400-410 °C and with LHSV of 03-05 h-1. It took about 400 h for the catalyst to reach stable activity, after which almost constant yields were obtained until the end of the reaction.[21]

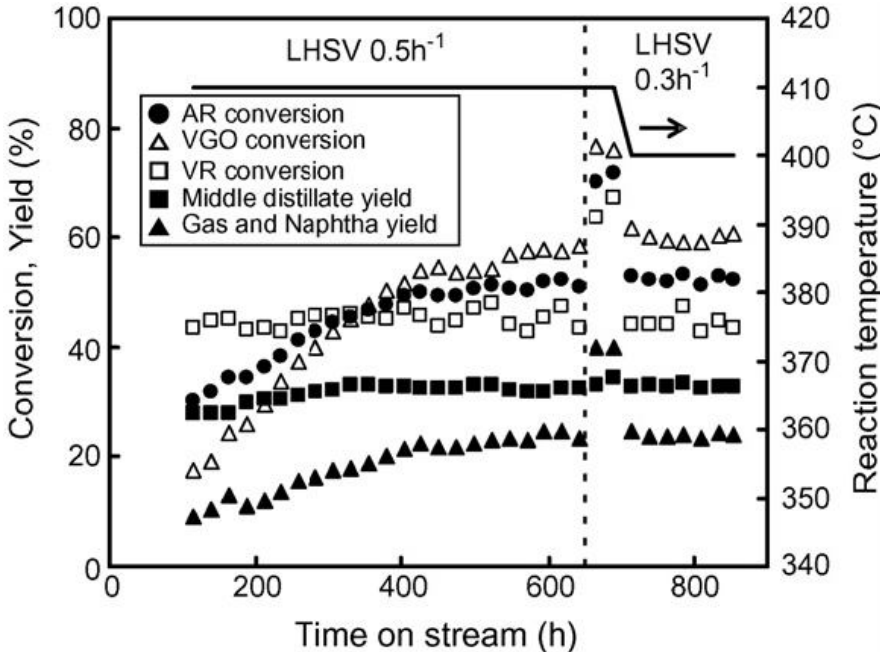

Figure 2: Change in catalytic activity of NiMo/MTZ-N1 with time on stream [21]

Šimaček i Kubička[22] studied hydrocracking of pure petroleum vacuum distillate and the same fraction containing 5 wt.% of rapeseed oil over commercial NiMo/Al2O3 catalyst with the goal of obtaining higher middle distillate yields suitable for diesel production. The product of hydrocracking at 400 and 420 °C was distilled in order to isolate diesel fraction (gas oils and remixed blends of kerosene and gas oil) from naphtha fraction and from high-boiling hydrocarbons designated as residue. The yields of distillation are presented in Table 1. The replacement of 5% of vacuum distillate by rapeseed oil caused minor increase of the distillate fractions content. The reaction temperature plays, on the other hand, more important role, as can be seen by the dramatic increase of the kerosene yield when the reaction temperature was increased from 400 to 420 °C. Similar trend is also visible for the gas-oil yield while the residue yield decreased but the loses increased. Obtained gas oils contained more than 5 wt.% of hydrocarbon-based biodiesel. The products contained neither free fatty acids nor triglycerides (products of incomplete transformation of rapeseed oil into hydrocarbons). Larger formation of i-alkanes at 420 °C decreased the content of n-heptadecane and n-octadecane in the co-processed product. Consequently, the key low-temperature properties of this product were significantly improved. It seems that joint hydrocracking of petroleum raw

material and vegetable oil can be a promising alternative to produce green diesel using existing refinery technologies.[22]

Table 1: Distillation yields of the products obtained by hydrocracking (at 400 and 420 °C) of vacuum distillate (VD) and vacuum distillate containing 5 wt.% of rapeseed oil (RO) [22]

Parameter	Yield, %			
	VD (400 °C)	VD + RO (400 °C)	VD (420 °C)	VD + RO (420 °C)
Kerosene	5.3	6.4	18.1	19.8
Gas oil	41.9	45.6	53.9	55.4
Residue	52.4	47.2	26.6	23.2
Losses	0.4	0.9	1.4	1.6

Guzman et. al[23] conducted hydroprocessing of palm oil in a pilot-plant using conventional hydrotreating catalyst (NiMo/g-Al_2O_3). At 40–90 bar hydrogen pressure crude palm oil (CPO) can be deeply converted into paraffins in the diesel range. Table 2 shows properties of crude palm oil (CPO) and hydrogenation products at different time on stream. As can be seen from this data the product even at the longest time on stream monitored consists of a fuel that fulfills most of the specifications required for a diesel. The GC-MS analysis of the obtained products showed that the content of heavy organic oxygen containing compounds increased with time. Components as octadecanol, n-hexadecanoic acid, octadecanal, and the esters hexadecyl hexadecanoate and octadecyl hexadecanoate were identified. The presence of these heavy oxygen containing components has been interpreted as a slight deactivation of the catalysts that leads to a gradual lost of selectivity to the main C15–C18 products that constitute the renewable diesel. However, for an industrial application this can be overcome by operating the plant at higher pressures and by co-processing with crude oil diesel. Both strategies will permit to use conventional catalyst as the one tested in this study in the existing hydrotreating facilities at the refineries.[23]

Table 2: Properties of crude palm oil (CPO) and hydrogenation products at different time on stream [23]

Property	CPO	Time on stream, h				
		1	4	9	11	16
Cetane index, -	-	96.1	95.1	94.4	93.4	92.5
Kinematic viscosity at 40 °C, $mm^2\ s^{-1}$	39.8423	3.3931	3.523	3.5464	3.627	3.6918
Density at 15 8C, $g\ cm^{-3}$	0.9152	0.7839	0.7855	0.7856	0.7872	0.7882
API, °API	23.0	48.9	48.6	48.6	48.2	48.0
Color, -	5.5	0.6	0.6	0.7	0.8	0.7
Thermal stability, % reflectancy	98	99	99	98	99	99
Bromine number, g Br_2/100 g	-	3.85	4.28	5.05	6.26	5.75

2.2 Alkylation

Alkylation is a well known refinery process for converting C3-C5 olefins and iso-butane into C5-C12 highly branched iso-paraffins which together form alkylate. The value of alkylate as a gasoline blending component has significantly risen in recent times. The reactions that occur during the process of alkylation include addition of low molecular weight alkenes and alkanes which result in formations of higher molecular weight branched iso-alkanes with very high octane numbers. The fact that alkylate does not contain olefins or aromatic, sulfur and nitrogen compounds makes it environmentally friendly gasoline blending component.

However, conventional alkylation technology are not entirely environmentally acceptable because they use as catalysts large amounts of sulfuric or hydrofluoric acid which present potential sources of toxic waste and are direct safety threat. New processes are being developed and research carried out in order to enable the alkylation processing in a more environmentally friendly way and safely and the main goal is to enable the efficient application of solid catalysts.[11,18,24]

An alkylation process that employs solid acid catalyst similar to those used for hydroprocessing was commercially applied in a refinery. During this process olefins react with isobutane on the surface of the catalyst to form a complex mixture of highly branched isoalkanes called alkylate. The key reaction step is the protonation of a light olefin on the solid catalyst surface followed by alkylation of an olefin on the C4 carbocation, forming the C8 carbocation. This process does not produce acid-soluble oil. Also, it has minimal polymerization, and the alkylate has lighter distillation properties than alkylate from HF or H_2SO_4 liquid acid technologies. Polymerization to acid-soluble oil (ASO) is found in liquid acid technologies and results in additional catalyst consumption and yield loss. The properties of alkylate are similar to the products from alkylation process using liquid acid catalysts and even better in some regards as can be seen on Fig. 3. The process can be efficiently carried out at relatively low process temperature of 25 °C with high local isobutene/olefin ratio and short contact time between the reactant and catalyst when higher iso-octane that is 2,2,3-trimethylpentane yields can be obtained. The yields of 2,2- dimethylhexane which is undesirable because of lower-octane blend values are decreased. Process conditions are mild and do not require expensive or exotic metallurgy.[25]

The schematic of this proces is shown on Fig. 4. Feeds to the unit are dried and pretreated to move impurities and contaminants such as diolefins, oxygenates, nitrogen, and sulfur. These contaminants also cause higher acid consumption, higher acid-soluble oil formation, and lower acid strength in liquid acid technologies. The olefin and isobutane are combined and injected into a carbon-steel riser reactor with continuous catalyst reactivation to maintain a constant catalyst activity and minimize catalyst inventory. This provides constant product quality, high yield, and high on-stream efficiency.

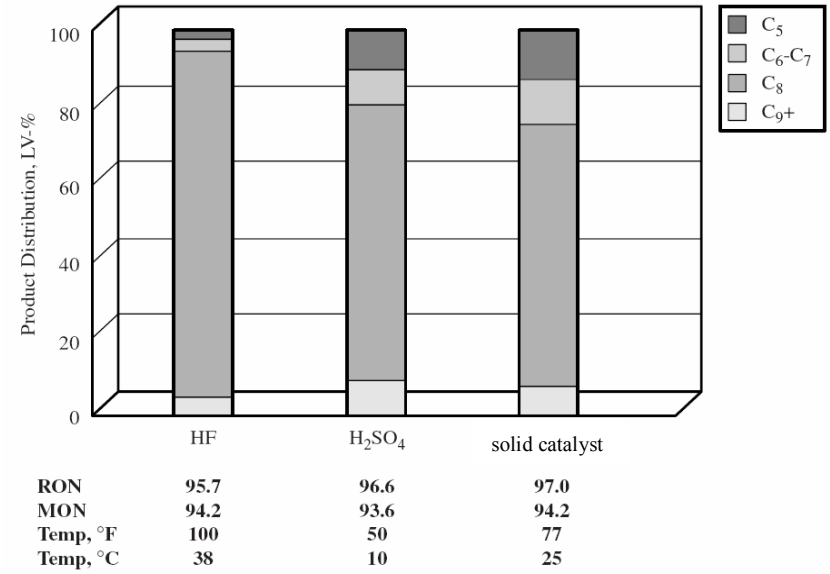

Figure 3: Catalyst comparison: mixed 4 olefin feed[25]

Liquid-phase hydrocarbon reactants transport the catalyst around the reactor circuit where velocities are low relative to those of other moving catalyst processes. The catalyst and hydrocarbon are intimately mixed during the reaction, and the catalyst is easily disengaged from the hydrocarbon product at the top of the reactor. Alkylate from the reactor is sent to a downstream fractionation section, which is similar to fractionation sections in liquid acid process flow schemes. The fractionation section recycles the unconverted isobutane back to the reactor and separates out the final alkylate product. The catalyst is reactivated by a simple hydrogenation of the heavier alkylate on the catalyst in the reactivation wash zone. Hydrogen consumption is minimal as the quantity of heavy alkylate on the catalyst is very small. A small catalyst slipstream flows into a separate vessel for reactivation in vapor phase with relatively mild conditions to remove any last traces of heavy material and return the catalyst activity to essentially the activity of fresh catalyst. The reaction time is on the order of minutes for the completion of the primary reactions and to minimize secondary reactions. This process has a yield advantage over liquid acid alkylation technologies and does not produce acid-soluble oil by-products. In addition, the capital cost of this process is competitive compared with existing technologies, and maintenance costs are lower. The HF alkylation unit requires HF mitigation capital and operating costs. The sulfuric acid alkylation unit requires regeneration or transport of large volumes of acid. Overall, this process is a safe and competitive option for today's refiner.[25]

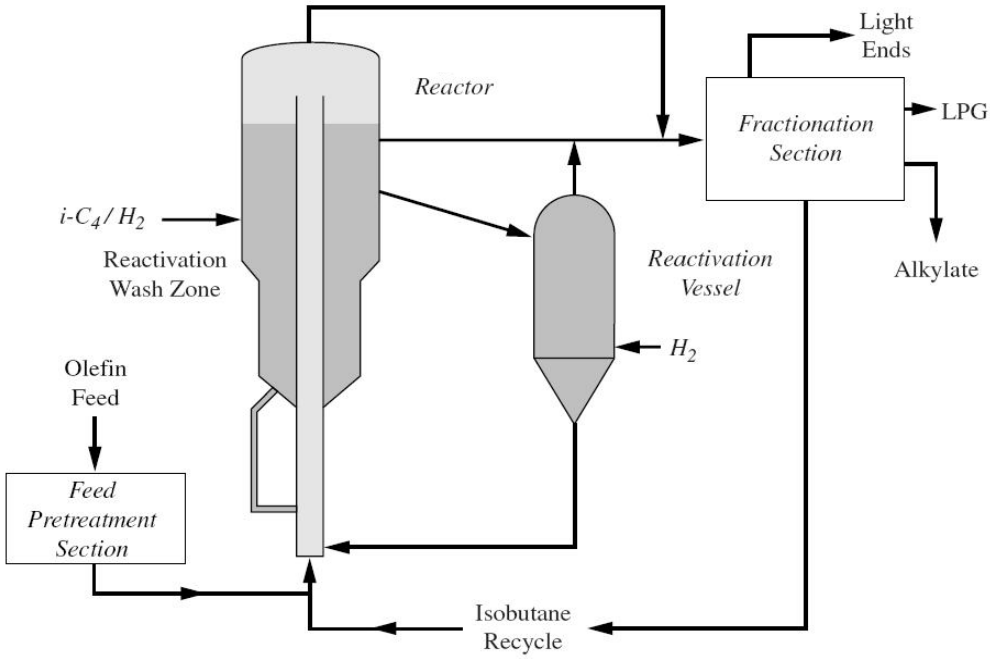

Figure 4: Solid catalyst process flow diagram[25]

Another commercially available alkylation process that employs solid acid catalyst was developed but has not yet been implemented as a larger capacity refinery unit. This process is carried out on an acid zeolite catalyst at elevated temperatures of 50-90 °C. The product is high-quality sulfur free alkylate (96 octane) without acid-soluble oils. The catalyst is a solid, non corrosive material which is easily transported and stored. The process is conducted in a fixed-bed reactor and slow catalyst deactivation does occur, mainly due to formation of small amounts of heavy by-products which clog the catalyst pores.

To solve this problem, the process uses multiple reactors, with individual reactors cycling back and forth between on-line alkylation and mild catalyst regeneration (in hydrogen stream and at process temperature). However, under these conditions the full recovery of the catalyst activity is not achivable.[26] After a period of time the process must be stopped and regeneration conducted at high temperatures of around 250 °C and in the presence of hydrogen when the olefin addition reactions are stopped and heavy alkylates are removed from the surface of the catalyst. The schematic of this process, shown on Fig. 5, comprises three reactors which are used simultaneously for conducting all three phases of the process ensuring continuous processing. The fact that catalyst does not have to be moved from the reactors

during the alkylation and two regeneration stages facilitates processing continuity. Zeolite catalyst does not contain halogens or volatile components and has low sensitivity towards feedstock composition variation and common impurities such as water, oxygenates sulfur compounds or butadiene. Should catalyst come in to contact with these impurities they would not cause permanent deactivation, although by pretreating the feed longer catalysts life cycle and activity as well as better product quality would be achieved. Economic analysis and estimation showed this process to be competitive in relation to the liquid acid alkylation processes with the reduced safety and environmental risks.[27]

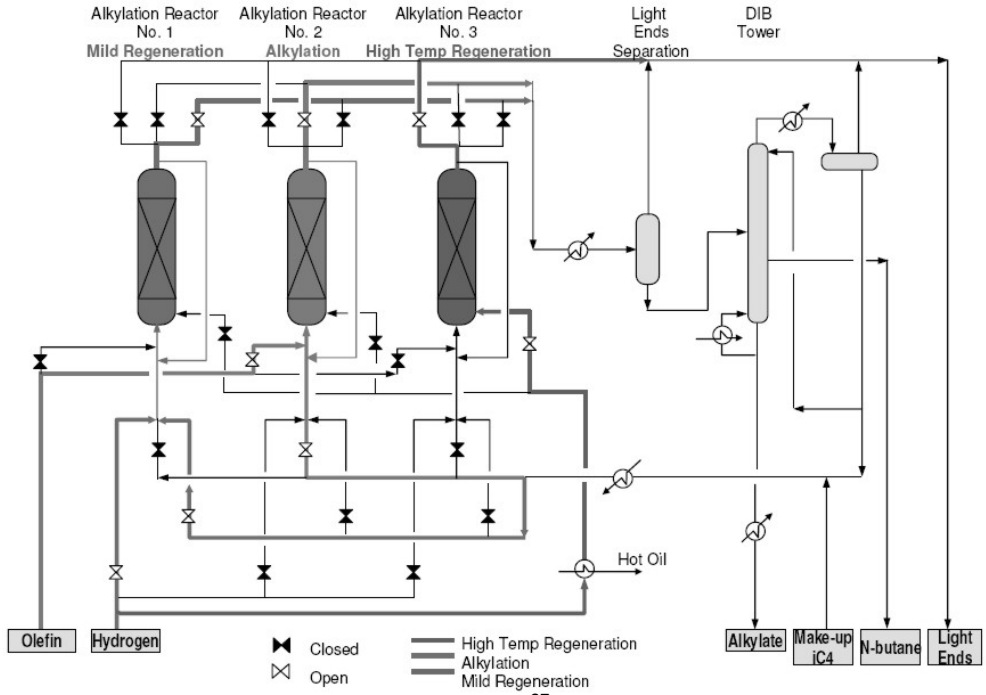

Figure 5: Solid catalyst process flow diagram.[27]

The cost comparison between this process and conventional H_2SO_4 catalyst alkylation process (Table 3) shows that for approximately the same cost one can produce roughly the same quality alkylate but with significantly reduced immediate risks and indirect environmental impact.[27]

Dalla Costa i Querini[28] studied the beta and Y zeolites as a solid acid catalysts for the alkylation of isobutane (iC4) with C4 olefins (C4=). Beta zeolite possesses relatively high density of Brönsted acid sites and favorable pore structure. The alkylation reaction was carried out in a fixed bed reactor, at 30 atm and 80 °C, with a

molar ratio isobutane/C4 olefins = 15. The experiments were carried out with beta zeolites in protonic form (B-H), in the form of partially (B-LCH) and fully (B-LCL) exchanged with La and in the forms with added Pt (Pt-B-H, Pt-B-LCH), as well as with Y zeolites in protonic form (Y-H), in the form of partially exchanged with La (Y-LCH) and in the form with added Pt (Pt-Y-LCH).

Table 3: Comparative economics of alkylation process shown in Fig. 5 (ZCAT) and conventional H_2SO_4 catalyst alkylation process[27]

Process		ZCAT	H_2SO_4
Alkylate Capacity, BPSD		10,000	10,000
Alkylate RON, -		95.0 -96.0	95.0 -96.0
Estimated ISBL TIC,, US $ * 10^6		31.0	36.5
Production Costs, $/bbl	Variable Costs (Feeds – by-products + Cat./Chem. + Utilities)	21.74-22.24	20.82
	Fixed Costs (Labor + Maintenance + Ovhd. + Insurance + Misc. Indirects)	1.90	2.05
	Capital Costs (Depreciation+Return on Capital)	4.85	5.71
	Total Production Cost	28.49-28.99	28.58

Fig. 6 shows the distribution of trimethylpentane (TMP) in the C5+ fraction (including iso-pentane). It can be observed that Y-LCH zeolite presents the best yield in TMP. The beta zeolite in protonic and LCH forms presents a similar behavior, while when it is completely exchanged with La, (B-LCL), it has a lower activity.[28]

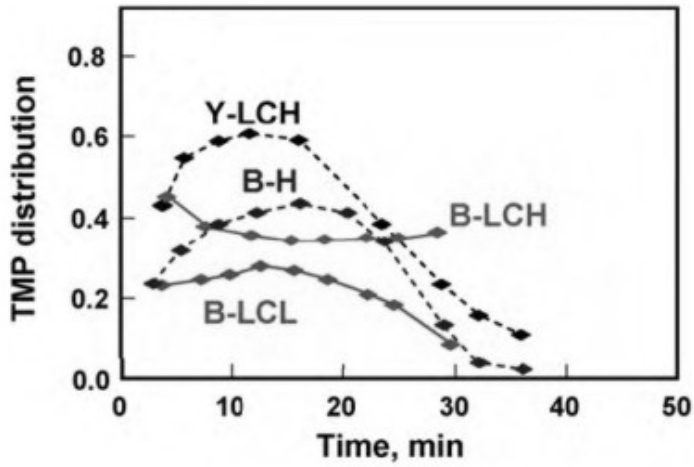

Figure 6: Content of TMPs in C5+ fraction for different catalysts[28]

In all cases, except with the B-LCH catalyst, a pronounced drop in the activity is observed, within 20–30 min times on stream. Since the B-LCH catalyst has a negligible amount of lanthanum, consequently its composition is quite similar to that of the B-H catalyst. The incorporation of platinum in the zeolite beta does not produce changes in the activity or stability of the catalyst, but makes it possible to regenerate the catalyst with hydrogen at low temperature (80 °C).[28]

Dalla Costa i Querini[29] studied the isobutane alkylation in gas phase using Y zeolite i mordenite catalysts. The alkylation reaction of isobutane with a mixture of C4 linear olefins was carried out in the gas phase at temperatures between 80 °C and 150 °C, and at atmospheric pressure, in a fixed-bed reactor. Experiments were carried out with Na-Y zeolite and mordenite (MOR) and with their exchanged forms only with La (LCL-Y, LCL-MOR) and exchanged with La i NH4+ (LCH-Y, LCH-MOR). High reaction temperatures lead to a very low production of branched C8 products at short reaction time, and as coke is deposited, the TMP production increases. In this way, the stability of the catalysts is improved. However, coke deposition decreases the cracking activity and the hydrogen transfer capacity. Process in which the temperature is increased during the reaction facilitates the possibility of larger improvement of the liquid yield and the concentration of TMPs in the liquid. Higher temperatures during the reaction also make it possible to slow down the pore mouth plugging, mainly due to a faster cracking rate of the hydrocarbons deposits. As a consequence, a better utilization of the internal surface takes place and a higher amount of coke can be observed when the reaction is carried out at higher temperature.[29]

The possibilities of applying alkylation for desulfurization of gasoline fuels are scientifically studied using solid catalysts. Guo et al.[30] studied alkylation reactions of thiophenic compounds over solid phosphoric acid catalysts (SPAM and SPAS using MCM-41 and Silicalite-1 zeolite as supporters respectively) and macroporous sulfonic resins (including NKC-9, D005-2 and Amberlyst 35) with model gasoline and FCC (fluid catalytic cracking) gasoline. Results showed that macroporous sulfonic resins showed better performance than solid phosphoric acid catalysts under milder conditions in both feeds. Resins were also found to be more active for the conversion of thiophenic compounds. Phosphoric acid catalyst showed different activity orders in model gasoline and FCC gasoline. High temperature was harmful to the product yield and catalyst stability.[30]

Arias et al.[15] studied the alkylation of 3-methylthiophene (3MT) with 2-methyl-2-butene (2M2B) and the alkylation of sulfur compounds in the real FCC gasoline feed using various solid acidic materials including silica-supported phosphoric acid, MCM-22, USY i Hbeta zeolites and silica-supported 12-phosphotungstic (HPW) and 12-silicotungstic (HSiW) hetropolyacids. The initial catalytic activities observed in batch reactor for the various catalytic materials are displayed in Fig. 7. It can be seen that silica-supported heteropolyacids are the most active catalysts. The H-Beta sample presents the highest activity among the considered zeolitic materials. The lowest activity was determined for MCM-22 and SPA-11 materials. The silica-

supported heteropolyacids lead selectively to products of dialkylation and proved to be less deactivated than the other solids in continuous tests. Then, they catalyzed efficiently the transformation of sulfur compounds in real feed of FCC gasoline under soft reaction conditions. In these experiments, benzothiophenic derivatives were preferentially converted than thiophenic compounds. Evidence for cracking reactions was found at the beginning of the catalytic test leading to the formation of S8. Catalyst deactivation, probably mainly due to the poisoning by N-compounds and coke deposition at the beginning of the reaction, may be drastically reduced by increasing the temperature of the reaction.[15]

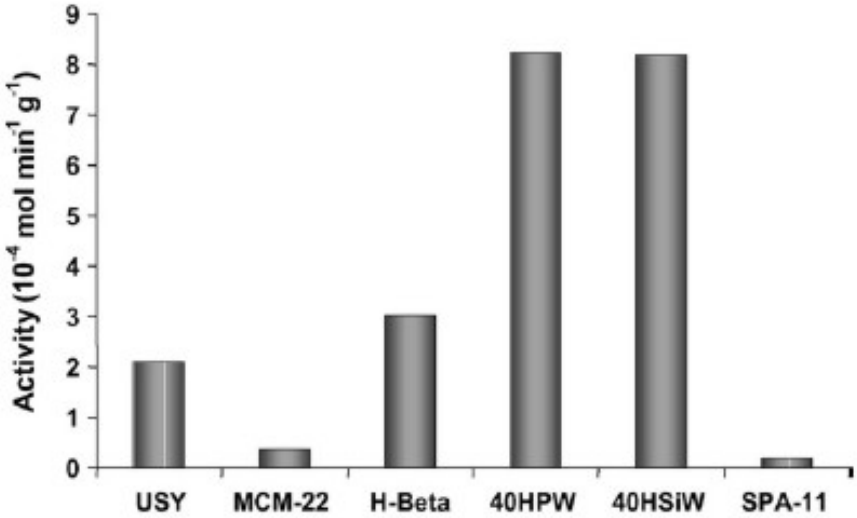

Figure 7: Initial activities in the alkylation of 3MT with 2M2B[15]

2.3 Isomerization

Isomerization is a conversion process which has been for more then 40 years used for converting n-alkanes into iso-alkanes. The product, i.e. the isomerizate is used as a gasoline blending component for enhancing octane number. The most commonly used feedstock for this process is a light gasoline which is mostly composed of n-pentane (C5) and n-hexane (C6). Demand for isomerizate is increasing and it is expected to continue raising due to the environmentally friendly nature of iso-alkanes as octane number boosters and because the isomerization is a cost effective way to control the aromatic content in motor gasolines.[18,31]

Many commercial catalysts and technologies currently exist for isomerization of light naphtha. In the current economic climate only the lowest capital solutions are desired. Figure 8 illustrates the comparison between available technologies on the basis of the performance, measured in octane-barrels, to the cost of the process, described by the ISBL EEC.[31]

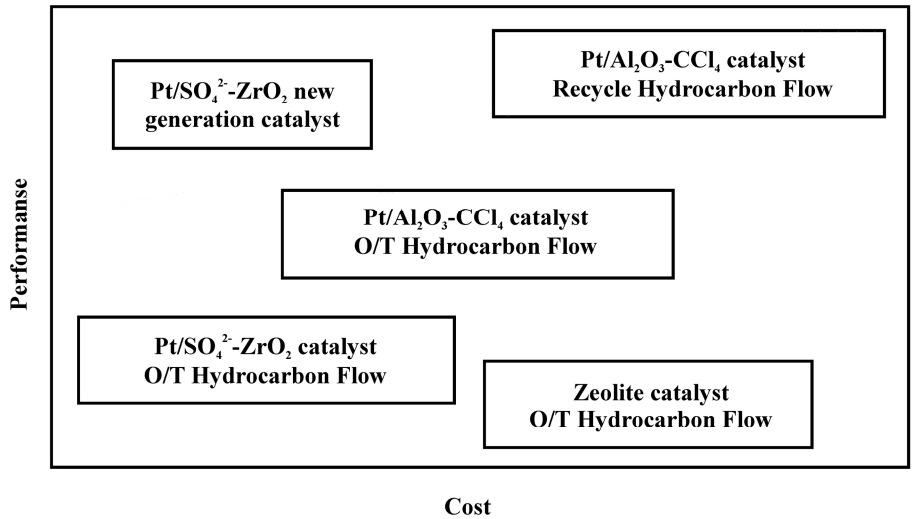

Figure 8: Relative cost vs. performance of light paraffin isomerization options[31]

The most widely used catalysts are Pt/Al_2O_3-CCl_4, so called chlorided-alumina catalysts that offer the highest activity and yield. However these catalysts are very sensitive to the presence of sulfur, nitrogen and water in the feed. The need for large amounts of carbon tetrachloride (CCl4) which is a dangerous compound for the humans and the environment a like makes this technology not environmentally friendly. That is why new isomerization technologies were and are being researched and developed which would be more environmentally friendly using less harmful chemicals during operation. The products of new technologies would have improved quality, i.e. isomerizate with higher octane number and lower sulfur and benzene content. There are two new types of commercially available catalysts Pt/SO_4^{2-}-ZrO_2, so called sulfated-zirconia catalysts, and Pt/zeolite catalysts. Technologies based on sulfated-zirconia catalysts have the lowest operating costs and are more active then the zeolite catalysts. The new generation of sulfated-zirconia catalysts has activity that approaches the activity of chlorided-alumina catalysts (Fig. 8).

Zeolite catalysts are structured in such away that they possess intrinsic acidity. They do not require an organic chloride co-feed for operation facilitating easier handling and removing a potential cause of corrosion. Zeolite catalysts are regenerable and relatively contaminant tolerant; the presence of water does not cause permanent catalyst deactivation. However, zeolite catalysts are the lowest activity catalyst family and their higher operating temperatures cause lower content of isomers in isomerizate.

Sulfated-zirconia catalysts also do not need an organic chloride co-feed for operation. The development of new generation of Pt/SO_4^{2-}-ZrO_2 catalysts facilitated the improvement in their regenerabilty and contaminant tolerance especially towards water, aromatics and sulfur. The new generation sulfated-zirconia catalysts make the building of a new unit or the conversion of an old isomerization/reformer unit very cost effective. The comparison between the technologies that use sulfated-zirconia and chlorided-alumina catalysts in relation to the product quality, product yield, and erected equipment costs (EEC) are shown in Table 4. It can be seen that chlorided-alumina technology produces isomerizate with slightly higher octane number (RON) and achieves higher yields but the erected equipment costs of sulfated-zirconia technology are lower.[31]

Table 4: Performance and cost comparison of unit conversion to Pt/Al_2O_3-CCl_4 and Pt/SO_4^{2-}-ZrO_2 technologies[31]

Process	RON, -	Yield, RON * bbls	EEC, 10^6 $
Hydrocarbon-once-through			
Pt/Al_2O_3-CCl_4	83.7	821,000	10.8
Pt/SO_4^{2-}-ZrO_2 (new generation catalyst)	81.4	796,000	7.8
Hydrocarbon-recycle (DIH)			
Pt/Al_2O_3-CCl_4	87.4	853,000	18.3
Pt/SO_4^{2-}-ZrO_2 (new generation catalyst)	87.0	805,000	14.0

Intensive scientific research is being carried out on new materials as alternative isomerization catalysts. Materials that are showing potential for commercial application include tungsten and molybdenum carbides and their combinations with oxides such as molybdenum carbide/tungsten oxide.[32]

Further research is being carried out on platinum based catalysts with addition of molybdenum oxide[33], HZSM-12[34] and Beta[35] zeolites, then on nickel based catalysts including nickel-HZSM-5 zeolites[36] i nickel-platinum-HUSY zeolites[37]. Research is also carried out on different forms of catalysts containing zirconia such as paladium-zirconia-sodiummontmorillonite-sulfate[38], platinum-iron-tungsten-zirconia-nitrate and platinum-iron-tungsten-zirkonia-sulfate[39].

3. Conclusion

This overview of recent advances in research and development of hydrocracking, alkylation and isomerization processes provides an insight into the different opportunities for production of environmentally friendly fuel from petroleum fractions.

Hydrocracking process is being intensely researched and developed as one of the most valuable secondary refining processes for converting heavy hydrocarbon feeds such as heavy oils and residues and especially oils of plant origins. Different options for advancement in hydrocracking catalyst formulations are being explored towards

improving production efficiency for middle distillates and gasoline with satisfactory application properties including high octane/cetane number and low aromatics and sulfur content.

Research and development of alkylation process as a source of high octane and environmentally friendly gasoline blending component are primarily aimed at improving and finding new solid catalysts that would replace liquid catalytic systems. The new solid catalysts should be able to improve the safety and reduce environmental risks of the alkylation process while maintaining if not improving alkylate quality and yields. There are two new solid catalyst technologies commercially available of which one is already used in a large capacity refinery unit while the other is in use as a demonstration unit. Both technologies have proved them selves as very economically competitive and their results with regard to product quality and yields and cost effectiveness are on par or even better then in relation to conventional technologies with greatly improved safety and environmental aspects as well. Alkylation has been shown as a possible alternative desulfurization process but further research is needed.

Isomerization is a process for production of environmentally friendly gasoline blending component and for the most part research is carried out on solving inadequacies of conventional catalysts in relation to high sensitivity towards contaminants and environmental and safety problems. New generation of sulfated-zirconia isomerization catalysts has been developed which are characterized by high efficiency, although not quite on the level of conventional chlorided-alumina catalysts, and improved tolerance towards water, sulfur and benzene as well as easy regeneration and handling and low toxicity.

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UDK	ključne riječi	key words
665.7.035.7	ekološka prihvatljivost naftnih produkata	ecologic acceptability of petroleum products
614.7	zaštita okoliša	enviroment protection
665.642.6	hidrokrekiranje	hydrocracking
665.652.4	alkilacija	alkylation
665.656.2	izomerizacija	isomerization
665.625	predobrada ulazne sirovine	feedstock pretreatmment

Authors
dr. sc. Marko Mužic, e-mail: mmuzic@fkit.hr ; prof. dr. sc. Katica Sertić Bionda, Tamara Adžamić, dipl. ing.
Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia

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