The AlkyClean® Alkylation Process –
New Technology Eliminates Liquid Acids

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Introduction

Refiners now have available a cleaner and inherently safer alkylation technology, the AlkyClean® alkylation process. Based on over two years of successful operation of a prototype, refinery slipstream demonstration unit, the new process, employing an environmentally friendly zeolite catalyst, has proven to be a reliable and cost competitive alternative to existing liquid acid technologies.

The new solid acid catalyst (SAC) process produces high quality alkylate without all the drawbacks of the existing hydrofluoric (HF) and sulfuric (H_2SO_4) acid based technologies. Neither acid soluble oils (ASO) nor spent acids are produced, and there is no need for product post-treatment of any kind. Besides these processing advantages, eliminating the use of these toxic and corrosive liquid acids greatly reduces maintenance and monitoring requirements while reducing environmental and personnel safety concerns. Benchmarking efforts have confirmed the overall competitiveness of the new technology.

Alkylate, the product of the reaction of isobutane with light olefins (C_3-C_5), is highly valued as an ideal "clean fuels" blending component in the gasoline pool because it has no olefins or aromatic compounds, a low sulfur content, a limited heavy end, a low vapor pressure and both high research and motor octane numbers. As MTBE use further diminishes, alkylate will continue its growing importance as a means to compensate for lost octane-barrels and to recapture isobutylene back into the gasoline pool. Relative to catalytic polymerization (cat-poly), economic evaluation indicates that replacing an existing cat-poly unit with the AlkyClean process will result in a very attractive payout, which can be less than one year.

Process flow scheme

The process flow scheme for the AlkyClean process is similar to that employed for current liquid acid technologies. As illustrated in Figure 1, the process consists of four main sections: feedstock pretreatment, reactor system, catalyst regeneration, and product distillation.

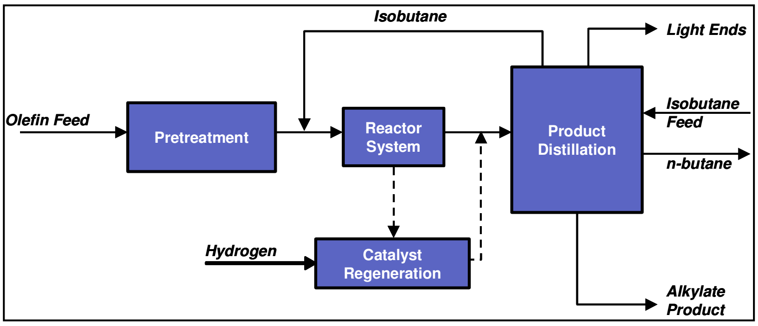

Figure 1. Simplified block diagram of the new AlkyClean process

Feedstock pretreatment requirements will depend on contaminant levels, but are generally expected to be no greater than those prudent for the liquid acids. The zeolite catalyst utilized in the process is rugged, with a good tolerance to typical impurities. It is easily regenerated to its full activity in the event of an accidental exposure to high levels of contaminants.

Table 1 compares the process operating conditions for the AlkyClean process and the liquid acid technologies. The AlkyClean reactor system operates in the liquid phase at higher temperatures, in the range of 50-90°C (122-194°F), thereby, eliminating the costly refrigeration requirements associated with H_2SO_4 processes. To achieve a high octane alkylate and limit by-product production, H_2SO_4 units typically utilize a total reaction section (external) isobutene-to-olefin feed ratio (I/O) of between 8/1 and 10/1, while HF units optimally run at an I/O of between 12/1 and 15/1. With similar quality alkylate product, the I/O for the new SAC process is in the same range of that utilized for these liquid acid processes. The ability to operate the AlkyClean process at comparable I/O is important in two ways. First, it allows for a cost competitive process, as the fractionation requirements associated with isobutane recycle are major capital investment and operating cost components. Second, it facilitates incorporation of the technology in the revamp/de-bottlenecking of an existing liquid acid unit, potentially without major modification to the ‘back-end’ fractionation/recycle facilities.

Table 1
Operating conditions comparison

	AlkyClean Process	**H_2SO_4**	**HF**
Operating temperature	50-90°C (122-194°F)	4-10°C (39-50°F)	32-38°C (90-100°F)
External I/O	8-15/1	8-10/1	12-15/1

Catalyst

Central to the new technology is the utilization of a novel, “true” SAC. In this situation, “true” SAC means that the catalytic acid function is intrinsic to the solid itself rather than being a separate component, such as an immobilized liquid deposited on a solid substrate. The proprietary formulation is zeolite based. It contains no halogens, has acid sites with sufficient strength for alkylation, yields high quality alkylate with good selectivity, and exhibits the required activity, stability and regenerability characteristics necessary for a successful process. Most recently, this catalyst has been further optimized and successfully manufactured in commercial-scale trials. This optimization, a result of novel discoveries, has significantly increased catalyst activity.

Reactor system and cyclic operation with integrated catalyst regeneration

The AlkyClean process achieves superior performance by coupling its optimized SAC with an alkylation reactor system that efficiently minimizes the peak olefin concentration in the reaction zone (i.e., maximizes the internal I/O). This is accomplished by utilizing serial reaction stages and a unique, easily operable reactor design that achieves the operating conditions essential to attain high product quality and prevent rapid catalyst deactivation.

In the AlkyClean process, multiple reactors are used to allow for continuous alkylate production as individual reactors cycle back and forth between on-line alkylation and rejuvenation following an inventive procedure established during the process development effort.(1) During rejuvenation, olefin addition is stopped and hydrogen is added to achieve a low reactor concentration of dissolved hydrogen, while maintaining liquid phase alkylation reaction conditions. This allows for a seamless switchover between operations and minimizes energy consumption. The rejuvenation step serves to remove accumulating heavier molecular weight species that lead to catalyst pore plugging and deactivation. Over time, however, there is a gradual loss of catalyst activity. To fully recover this activity – with a frequency depending on the operating severity – a reactor is taken off-stream for a moderate temperature (250°C/482°F), vapor phase regeneration with hydrogen. To allow for this hydrogen strip/moderate temperature regeneration (MTR) operation while maintaining full continuous alkylate production, an additional swing reactor is provided.

This cyclic operation of the reactor section is depicted in the Figure 2. The process does not require any transfer of catalyst, either between reactor stages or to a separate regeneration vessel, thereby enhancing operability. The use of a swing reactor provides for additional maintenance flexibility and allows the unit to stay on-stream when catalyst replacement eventually becomes necessary after years of operation. At the end of its useful life, the catalyst is returnable to its manufacturer, eliminating any potential catalyst disposal problem for the refiner.

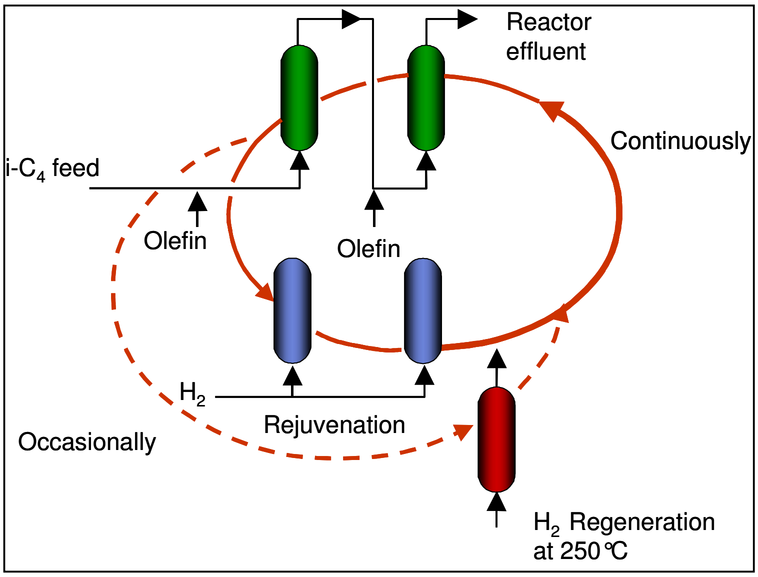

Figure 2: AlkyClean process reactor operating scheme

Demonstration Unit

Construction of a 10 BPSD AlkyClean process demonstration unit in Porvoo, Finland, was completed in 2002. Figure 3 shows the process flow schematic of the demonstration unit, which contains all of the key elements of a commercial plant. Three reactors are included, two under cyclic operation (i.e., alternating between alkylation and rejuvenation) allow for continuous production of alkylate, and the third allows for swing reactor MTR.

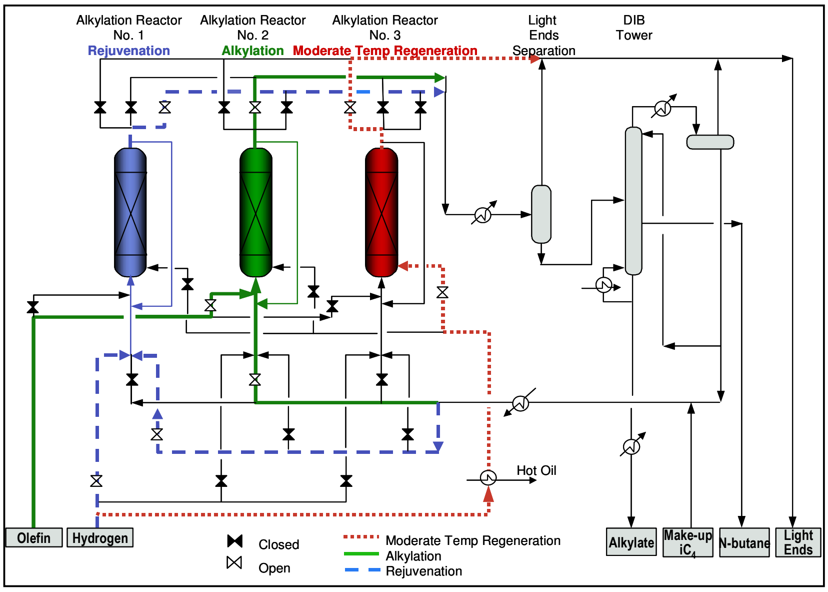

Figure 3: Process flow schematic of the demo unit

Figure 4 is a photograph of the installed reactor section. The reactors are sufficiently large and proportioned to allow for reliable scale-up. As such, each reactor represents a "core" of a much larger reactor and provides for the necessary hydrodynamic similarity to a full commercial-scale reactor system. Equally important to note, these reactors utilize SAC produced in commercial manufacturing trials, ensuring the exact catalyst characteristics of commercial-scale production conditions. Figure 5 provides an outside view of the facility, including the back-end deisobutanizer and alkylate product off-take trailer.

Figure 4: Demo reactor section

Figure 5: Demo unit outside view

Demonstration Unit Operation

After mechanical completion, the unit went through a shakeout and start-up period of about one month. During this period, procedures were refined and proven for the *in situ* activation of the catalyst and the reliable start-up of the reactor section. Subsequently, the unit operated reliably on a near continuous basis over several months utilizing piped slipstreams of the actual feeds processed in the nearby Porvoo Refinery HF alkylation unit, and produced alkylate of comparable high quality.

In addition to proving the operability of the process, key aspects of the technology were demonstrated. First and foremost was continuous cyclic operation – alternating reactors between periods of alkylation and rejuvenation – for periods of up to four weeks before taking a reactor off-line for MTR. In doing so, the durability of the catalyst was demonstrated over hundreds of cycles of rejuvenation and multiple MTRs. Regenerated catalyst samples from the unit were tested in a bench scale unit under benchmark conditions, further confirming the ability to repeatedly regenerate the catalyst and re-establish fresh catalyst activity and performance. After obtaining performance data over a wide range of conditions, which supported the identified objectives, the unit operation was temporarily suspended, allowing for unit modifications to incorporate identified operational improvements. During this hiatus, a newly improved catalyst was manufactured in a commercial scale trial and loaded into the reactors. Following these changes, the demonstration unit was restarted and ran smoothly and continuously for about six months under full cyclic operation, with periodic rotational MTR of the reactors. During this period, the benefits of the operational improvements were verified and the improved activity of the optimized AlkyClean catalyst was confirmed, along with stability and full activity recovery over multiple MTRs. Representative performance data from this latter operating period while processing refinery C_4 olefins are presented in Figures 6-8 for alkylate RON, RVP and C_5+ yield, respectively. This data, based on automated sampling from the on-line analytical system, show both the high product quality achieved and the stability of the cyclic process over time.

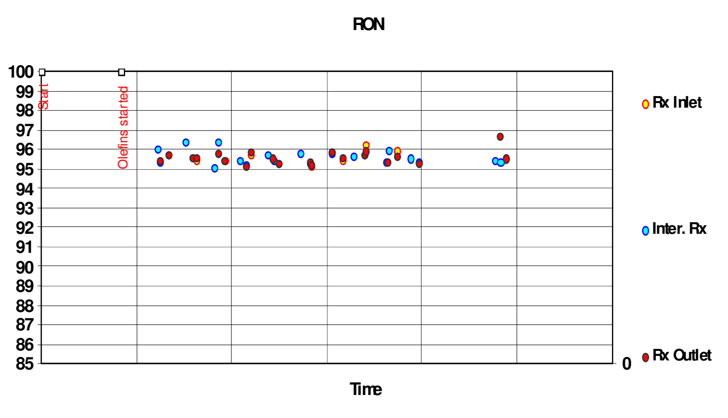

Figure 6: Demo unit performance processing refinery C_4 olefins, RON

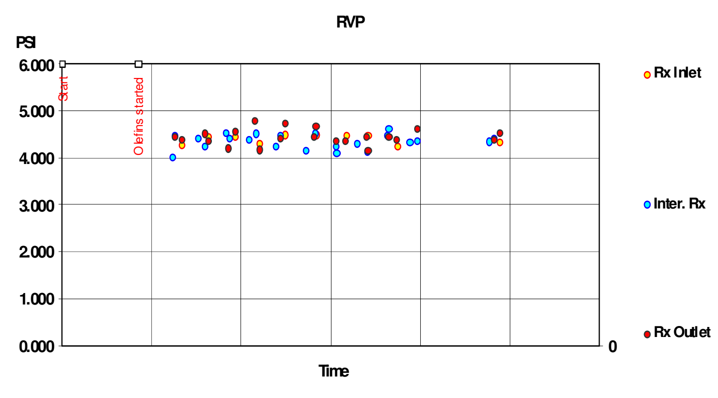

Figure 7: Demo unit performance processing refinery C_4 olefins, RVP

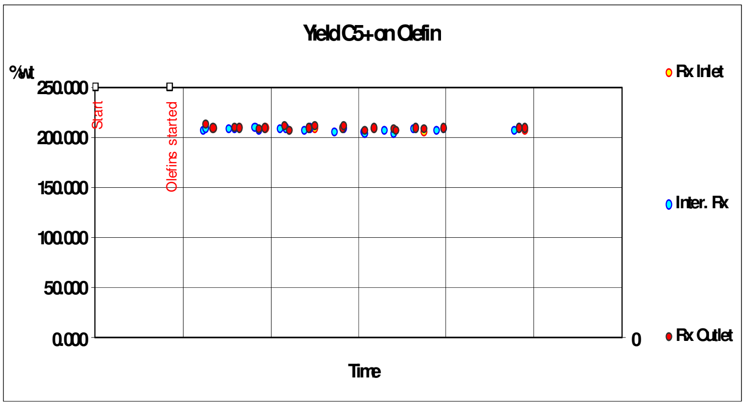

Figure 8: Demo unit performance processing refinery C_4 olefins, C_5+ yield on olefin

Competitiveness vs. liquid acid technologies

Table 2 provides an overview summary of the competitiveness of the AlkyClean process versus the established liquid acid technologies. The performance and economics of the AlkyClean process are fully competitive with current liquid acid technologies. High quality product has been reliably produced in an operation that has proven to be reliable and robust. Sensitivity to feedstock variation is low and tolerance to impurities is high. The economic competitiveness of the new SAC process is enhanced by its low mechanical complexity and the use of common (i.e. non-proprietary) refinery process equipment. The low pressure and mild temperatures employed, along with the absence of either a corrosive or erosive environment, allow for the use of carbon steel construction.

Based on an in-house benchmarking effort, we estimate that the total installed cost (TIC) for an AlkyClean process unit is about 10-15% lower than that for the equivalent H_2SO_4 unit. This comparison excludes off-site costs. When acid regeneration facilities for the H_2SO_4 unit are included, the SAC unit's cost becomes substantially less. We project that this level of investment for the SAC process is about on par with the cost for a HF unit. With respect to total cost of production, the results indicate that the requirements for the new AlkyClean process are comparable to that of the H_2SO_4 process. For both technologies, catalyst consumption cost is a significant component of the variable cost. In the case of the AlkyClean process**,** this cost was conservatively based on a minimum ultimate catalyst life. Thus, there is considerable upside potential, which would result in the reduction of the AlkyClean process's total production cost. In comparison to the AlkyClean and H_2SO_4 processes, production costs for HF units may be judged, on the surface, to still be somewhat lower; however, the increased costs for maintenance, mitigation, and monitoring, among others, that the HF technology requires offset any perceived advantage.

Table 2
Comparison of AlkyClean process with liquid acid technologies

Parameter	Modern Sulfuric Acid	Modern HF Acid	AlkyClean Process
Base Conditions:			
C_4= feedstock			
Product RON	95	95	95
Product MON	91.5	92.5	92.5
Alkylate Yield	Base	Base	Base or better
Total Installed Cost, ISBL	Base	85% of Base	85% of Base
Total Installed Cost Including OSBL (regeneration facilities, and/or safety installations)	Base	70% of Base	< 50% of Base
Feed Treatment	Base	Higher	Base
Product Treatment	Yes	Yes	No
ASO Yield	Base	Less	None
Equipment Maintenance	High	High	Very Low
Corrosion Problems	Yes	Yes	None
Reliability and On Stream Factor	Average	Average	Expected Above Average / High
Turnarounds Frequency / Duration	Varies / Longer	Varies / Longer	Match FCC or better / Shorter
OPEX	Base	Site Specific Typically Lower	Slightly Higher
OPEX with external regen (sulfuric)	Base	Site Specific Typically Lower	Base
Safety	Unit specific safety precautions as well as transport precautions	Very specific safety precautions required that extend throughout refinery	No special precautions other than those for any refinery process unit. Inert catalyst.
Environmental	-	-	No emissions to air, water, or ground.

Economic incentive for employing the AlkyClean process to replace cat-poly

Evaluation of the economics for replacing a cat-poly (or oligimerization) unit (and by extension other similar "indirect alkylation" units) with the AlkyClean process indicates a clear incentive for the installation of the SAC alkylation technology. The basis for this analysis was a typical C_4 FCC feed cut supporting the production of 10,000 BPSD of alkylate, with the corresponding production of cat-poly gasoline (at the same unit feed rate) falling out at 4,623 BPSD. Overall unit flow rates for cat-poly and the AlkyClean process are provided in the block flow diagrams of Figures 9 and 10, respectively. Two economic cases were developed based on historical U.S. Gulf Coast product pricing information derived from CMAI and Platt's. The first was a four-year average (spanning 2001-2005) and the second was for the single month at the end of this four year period, July 2005. For reference, this pricing information is summarized in Table 3.

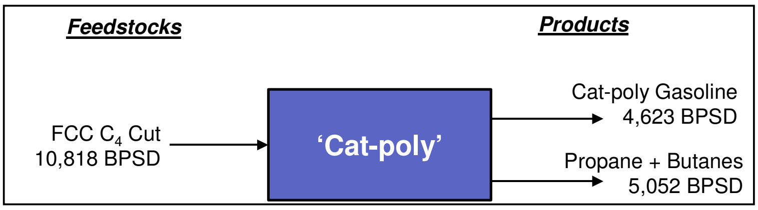

Figure 9: Cat-poly block flow diagram

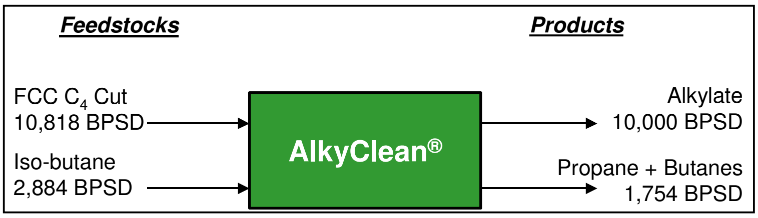

Figure 10: AlkyClean process block flow diagram

Table 3
Historical pricing information

	4 Year Average Case	Single Month Case (7/05)
	U.S. cents/gallon	
Propane	59.38	83.78
Iso-Butane	73.25	117.51
N-Butane	70.94	101.77
'Cat-poly'	99.49	166.02
Alkylate	111.99	186.24

The results of the evaluation for these two cases (i.e. four-year average and single month) are then summarized in Tables 4 and 5, respectively. In both cases, product slate values for the two processes are calculated net of operating costs and, additionally for the SAC alkylation process, net of supplemental isobutane make-up requirements. The net product slate value differential for the AlkyClean process relative to cat-poly was then calculated on a daily basis and converted to a yearly differential utilizing an on-stream factor of 350 operating days per annum. Finally, the simple payout period for the AlkyClean process investment was calculated based on the unit's in-house estimated total installed cost (TIC) of US$42 million (4th qtr. 2005, USGC location). Based on these calculations, the payouts in both cases are attractive. For the averaged four-year period, the payout is 1.7 years, and based on the single month period of July 2005, the payout is extremely low at only 0.9 years. The reduced payout time for the July 2005 period is not surprising, as it reflects last year's run-up in crude oil prices, which approached US$60 per barrel in July, relative to an average price of about US$35 per barrel for the four year period spanning 2001-2005. Finally, it should be noted that this analysis does not account for the blending advantage that alkylate offers relative to the highly olefinic cat-poly blendstock in terms of ability to produce additional volumes of RFG and CARB gasoline.

Table 4
AlkyClean vs. cat-poly – Four-year-average case

	Cat-poly	AlkyClean
	U.S. $/day	
Gasoline Blendstock	193,176	470,405
$C_3 + C_4$ By-products	152,232	51,561
Isobutane Make-up	-	(88,726)
Operating Cost	(16,002)	(34,213)
Net Product Slate Value	329,406	399,027
AlkyClean Differential	-	69,621
Annual AlkyClean Differential, MM$/yr.		24.4
AlkyClean TIC, MM$		42.0
AlkyClean Payout, yrs.		1.7

Table 5
AlkyClean vs. cat-poly – Single-month (7/05) case

	Cat-poly	AlkyClean
	U.S. $/day	
Gasoline Blendstock	322,354	782,286
$C_3 + C_4$ By-products	231,151	73,884
Isobutane Make-up	-	(142,338)
Operating Cost	(18,288)	(39,100)
Net Product Slate Value	535,217	674,732
AlkyClean Differential	-	139,515
Annual AlkyClean Differential, MM$/yr.		48.8
AlkyClean TIC, MM$		42.0
AlkyClean Payout, yrs.		0.9

Conclusions

The new AlkyClean solid acid catalyst alkylation process is now available to refiners and provides the following benefits:

- Elimination of corrosive / toxic liquid acid usage and associated safety concerns
- Elimination of heavy hydrocarbon by-product (ASO) production
- Elimination of reactor refrigeration and alloy construction material requirements
- High operating reliability and low maintenance costs
- Good tolerance to feedstock impurities
- Reduced sensitivity to changes in feedstock olefin composition
- Production of quality, high octane alkylate product
- Competitive plant investment and production costs
- Equipment reuse potential for more economical retrofitting/de-bottlenecking of existing liquid acid units
- Attractive payout potential for both new applications and as a replacement to catalytic polymerization units

This new “clean fuels” technology has successfully completed its demonstration phase. Spanning a period of more than two years, the many months of successful operation of the demonstration unit has confirmed all key aspects of the AlkyClean process technology, while allowing for both parametric optimization studies and the proofing of operational procedures to ensure the reliability of the new process. The unit operated on slipstreams from a nearby refinery and ultimately utilized an optimized, increased activity catalyst – which was successfully manufactured in a commercial scale trial – to fully prove the ‘real-world’ performance of the new SAC process.

Based on this effort, the AlkyClean process has proven to be robust, requiring minimal maintenance, while producing high quality product. The zeolite based solid acid catalyst has exhibited tolerance to both upsets and exposure to high levels of contaminants.The catalyst’s ability to be easily and repeatedly regenerated, with full activity recovery, has been demonstrated over long periods of operation. With all of its very positive benefits, this breakthrough technology provides a profitable addition to the processing portfolio of refiners, as they strive to meet regulatory-driven demand for both cleaner fuels and greener refining processes.

REFERENCES

1. Broekhoven, E.H. van, Mas Cabré, F.R., Bogaard, P., Klaver, G., Vonhof, M., US Patent No. 5.986.158 (1999).