

Removing acid droplets produced by alkylation reaction

Studies lead to a fuller understanding of how sulphuric acid droplets form in alkylation reactions and how to combat resulting downstream corrosion

DIWAKAR RANA, J RANDALL PETERSON and ROB EWING
DuPont Clean Technologies

Sulphuric acid alkylation technologies typically incorporate intense mixing of sulphuric acid (catalyst) with the hydrocarbon feeds to produce alkylate. Real world and laboratory experiments on Stratco alkylation equipment show that additional incremental mixing improves product quality and lowers catalyst consumption. But does more mixing in the reaction zone correlate to an increase in small droplets of entrained acid? Does reduced mixing intensity in the reaction zone correlate to a decrease in micron-sized droplets of entrained acid?

Recent research shows these same droplets exist regardless of the intensity of mixing, so effluent treating in addition to coalescing is necessary for their removal. Unit upsets, contaminants, increased throughput, propylene and high isobutylene feeds increase the need for effective effluent treating.

In this article, we provide a fresh perspective on the fundamental principles of acid droplet generation from the sulphuric acid alkylation reaction. Research by the University of Kansas shows that very small (~3 μm) and stable sulphuric acid droplets are formed during the actual reaction regardless of the mixing intensity.¹ The research team also found that intense reaction zone mixing does not increase the production of stable acid droplets nor the load on well-designed downstream separation and effluent treating equipment.¹

For the past several decades, common wisdom in sulphuric acid alkylation mostly blamed hydrocarbon-soluble esters in the net effluent for downstream corrosion and

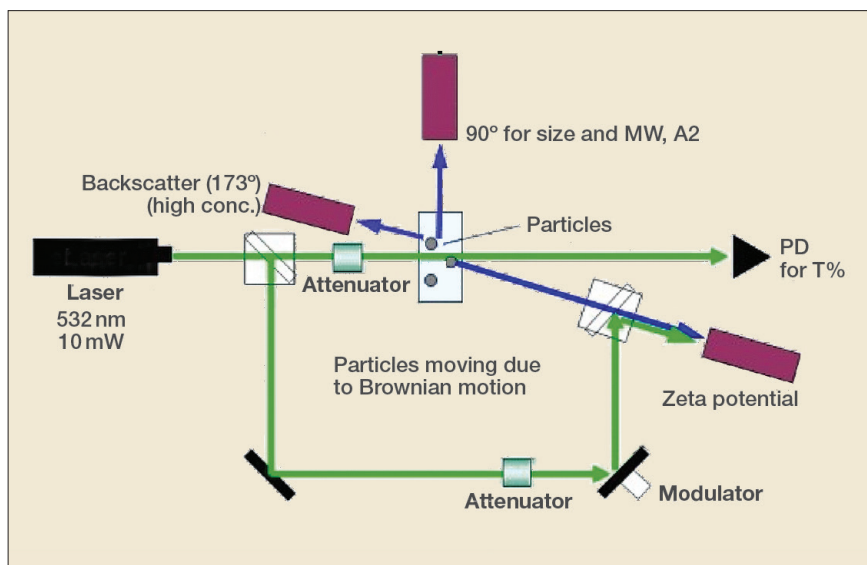


Figure 1 Dynamic light scattering (DLS) methodology to measure particle size of emulsions and colloidal suspensions with $\pm 2\%$ accuracy

fouling of equipment. DuPont Clean Technologies now believes that much of the trouble is caused by tiny droplets of acid that get past many effluent treating systems. All sulphuric acid alkylation reactors, no matter which technology, create 2-5 μm droplets of partially spent acid that entrains out of the reactor with the effluent. Since the droplets are very tiny, coalescers are not effective in their removal. It is therefore critical to treat the effluent to protect downstream equipment. The acid droplets contain acid soluble esters, while the clear hydrocarbon phase typically contains very few hydrocarbon soluble esters.

If the hydrocarbon phase is left untreated, these sulphuric acid droplets will degrade and turn into acid sludge and SO_2 within the fractionation section, thereby causing corrosion and fouling in the deisobutaniser overhead equipment

and reboiler. There is also a potential for these acid droplets to exit the unit with the alkylate product. Proper effluent treating can provide protection against corrosion and fouling in downstream equipment and vehicles, ensuring quality alkylate free from micron-sized emulsified acid droplets.

To take a deeper dive into how effluent treating serves its purpose, first and foremost it is important to understand what makes up the sulphur compounds in the reactor effluent and to examine the behaviour of the acid droplets in it. To this end, the University of Kansas employed a combination of state-of-the-art microscopic and analytical techniques to characterise weathered effluent (alkylate) as described below.

Reactor effluent analysis

Reactor effluent from the alkylation pilot plant in DuPont's Alkylation

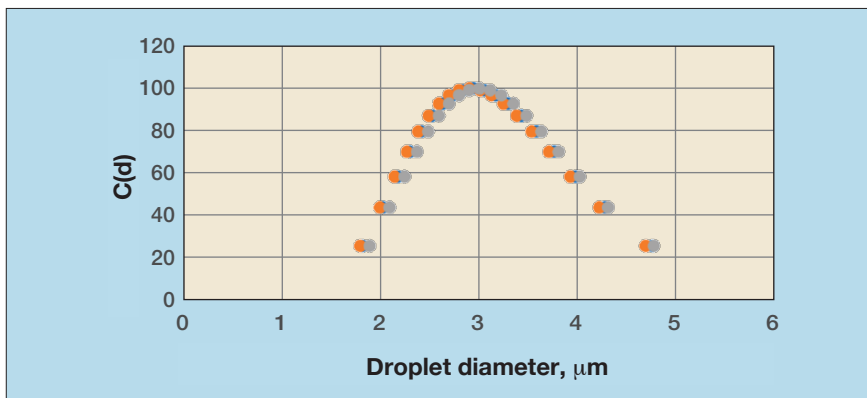


Figure 2 DLS size distribution of droplets within an untreated alkylate sample. Three replicates are shown

Technology Center was collected, then allowed to weather at $\sim 90^\circ\text{F}$ (32°C) to evaporate the butanes and other light hydrocarbons. The alkylate was otherwise untreated. The University of Kansas analysed these samples using dynamic light scattering (DLS) and optical microscopy. DLS identifies droplets in emulsion by measuring the diffraction of light as a laser passes through the sample (see **Figure 1**). DLS showed the presence of emulsified droplets which could not be separated from the alkylate even after days or months of gravity settling.

The results showed the presence of $2\text{--}5\ \mu\text{m}$ spherical droplets (see **Figure 2**).

A sulphur mass balance was performed on several samples. Knowing the total sulphur content of the untreated alkylate (both hydrocarbon and water soluble), it was water washed to extract the water soluble sulphur species. The water phase was analysed using the total acid number (TAN) titration method and the washed alkylate was analysed for total sulphur content. The sulphur mass balance typically closed within 3%. The sulphur species in the alkylate were analysed using mass spectrometry and a soft ionisation technique called CI-HEX. Secondary butyl sulphate was found in alkylate produced from butylene, and isopropyl sulphate was found in propylene alkylate. We suspect that these components act as surfactants and contribute to the stable acid emulsions in the hydrocarbon phase.

Regardless of the exact mechanism, these droplets are very stable

and do not separate out from the alkylate phase even when left to settle for months. They are also very acidic with a sulphur to oxygen ratio close to that expected for SO_4 .

On the basis of these results, sulphuric acid exists in the alkylate phase as part of a tight emulsion stabilised by the presence of alkyl sulphate.

The acid droplets, approximately $3\ \mu\text{m}$ in size (see **Figure 3**), do not coalesce but rather form larger agglomerate droplets when the alkylate is vacuum flashed (see **Figure 4**). These agglomerated droplets can easily be broken apart to their original disperse state by sonication for a few seconds. We believe that turbulent flow through piping in a commercial unit will keep the droplets from agglomerating.

Another interesting discovery made by the University of Kansas research team was that, when untreated alkylate is pressured through a $0.2\ \mu\text{m}$ syringe filter, the acid droplets are not coalesced nor strained out but rather squeeze through the pores and are reduced to $\sim 0.8\ \mu\text{m}$ immediately afterwards. Within 18 hours, however, the droplets return to their preferred $\sim 3\ \mu\text{m}$ size.

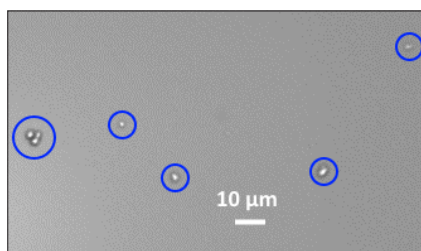


Figure 3 Photo showing isolated, sparse droplets in alkylate with droplet size $3\ \mu\text{m} \pm 1$

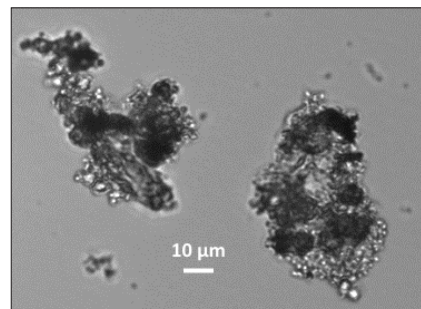


Figure 4 Photo showing the isolated droplets forming larger agglomerate droplets when vacuum flashed

Testing the hypothesis

Experiments were conducted at various mixing speeds: intense mixing – 25% more mixing speed, and mild mixing – 50% less mixing. The results from these experiments indicated that the size of these acid droplets was also $2\text{--}5\ \mu\text{m}$ when analysed using DLS techniques. Other experiments were conducted using a propylene feed which produces a more stable (tighter) emulsion compared to butylene. The sulphur content and quantity of droplets was greater but the size of the acid droplets was still found to be mostly within the $2\text{--}5\ \mu\text{m}$ range. We also collected untreated net effluent from a commercial Stratco alkylation unit which contained similar tiny acid droplets.

A new set of experiments was designed to synthetically create these acid droplets by intensely mixing sulphuric acid (either fresh or spent) with treated alkylate (containing no acid droplets) for 48 hours. However, no stable acid droplets were observed by DLS after 60 minutes of settling. Also, the resulting sulphur content was below the level of detection ($<0.3\ \text{ppm}$) which proves that sulphuric acid is not soluble in alkylate.

To summarise the findings, when alkylate is produced in a reaction, stable acid droplets of approximately $3\ \mu\text{m}$ in size are formed, no matter the mixing intensity or type of olefin feed. But when the University of Kansas team tried to create similar droplets within treated alkylate under intense mixing but with no chemical reaction occurring, they were unsuccessful. Past work published by Koch-Glitsch² reports that chemical reactions typically produce fine droplets ($<10\ \mu\text{m}$),

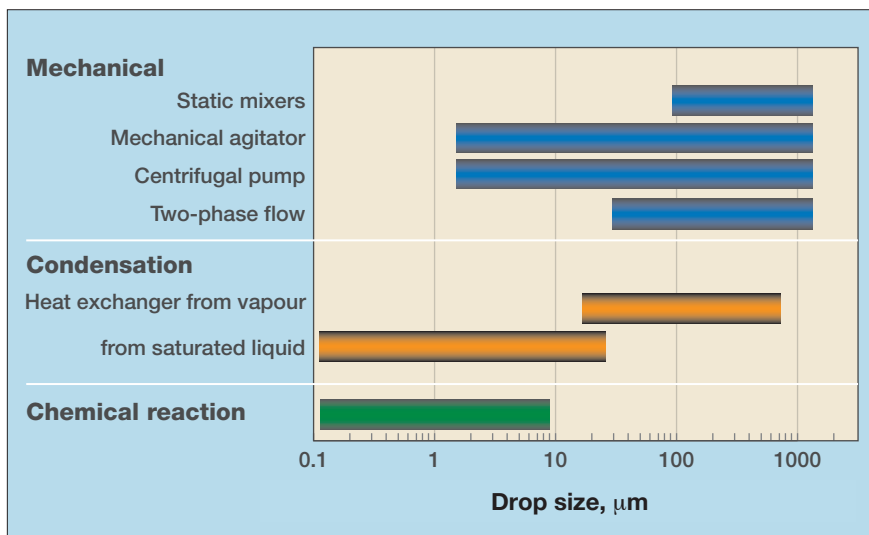


Figure 5 Typical droplet size ranges for various mechanisms³

whereas intense mechanical agitation creates droplets that are much bigger in size (see Figure 5).³

Intense mixing is beneficial to the alkylation reaction by increasing the surface area and mass transfer between the two phases. The above-mentioned experiments demonstrate that intense mixing alone is unable to create stable emulsified droplets. We deduce that chemical reactions involving the olefin, iso-paraffin and acid play an important role in the formation of stable droplets within the alkylation phase.

Effluent treating

Dry activated alumina treating

Based on what DuPont Clean Technologies has learned in the field and in the pilot plant, our current standard design has changed to dry activated alumina treating in order to capture and remove even the tiniest acid droplets. The net effluent first passes through an acid coalescer that is designed to recover >99% of the acid droplets that are larger than 10 μm. Coalescers are not very effective in removing droplets less than 6 μm – the majority of the stable acid droplets formed during the alkylation reaction.

The effluent then passes through a bed of activated alumina where the adsorbent reacts with and removes any acid that carries over from the acid coalescer. Esters and other reaction intermediates present in the net effluent are adsorbed onto the alumina. Alumina has proven to

be very effective in removing these components.

As an added benefit, the deisobutaniser runs dry as does the recycle isobutane stream. Refiners with alumina treating typically experience less corrosion in the reaction zone due to less water in the acid.

Typically, there are two beds – one in operation and one in standby or regeneration (see Figure 6). The beds are switched based on measured sulphur in the alkylate or simply based on time in operation, with the standby bed going into operation and the recently shutdown bed either being discarded or regenerated. The changeover frequency can be longer than six months depending on the design philosophy of the unit and the amount of entrained

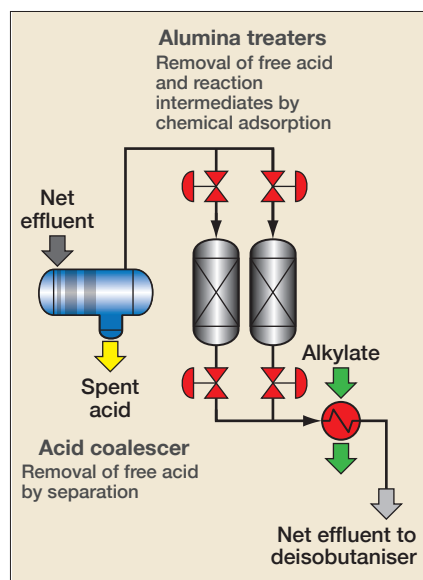


Figure 6 Stratco dry alumina treating system

acid and other sulphur components leaving the acid coalescer.

Wet effluent treating

Figure 7 illustrates the current Stratco wet effluent treatment system. The effluent first passes through the acid coalescer to remove >99% of acid droplets larger than 10 μm. It is then contacted with hot alkaline water within a static mixer to neutralise any remaining acid species. A water wash static mixer and coalescer are used to remove any salts that could plug the deisobutaniser.

Properly designed static mixers as well as adequate circulation and temperature are required to completely break down the acidic species to avoid downstream corrosion and fouling. The deisobutaniser feed and overhead recycle are saturated with water in this configuration, so more reaction zone corrosion is to be expected due to the higher water content in the acid.

We do not recommend bringing fresh acid into the acid coalescer or circulating acid through a static mixer as part of an acid wash. We have largely found this practice to be detrimental as it frequently increases the quantity of acidic species that the downstream equipment has to remove. Caustic consumption is much lower with an acid coalescer compared with an acid wash.

Conclusion

Throughout the history of sulphuric acid alkylation, separation of the hydrocarbon and acid phases has been an important part of the alkylation unit design. But we now better understand the mechanisms producing the various droplets within the two phases.

Small hydrocarbon droplets in the bulk acid emulsion are beneficial as they provide the necessary interfacial surface area for optimum alkylation reactions. Increased mixing decreases the average hydrocarbon droplet size but greatly increases the quantity of droplets and total surface area for desirable reactions to occur. However, increased mixing does not increase the quantity or decrease the size of the acid droplets within the hydrocarbon phase.

The 2-5 μm acid droplets found within the hydrocarbon phase are formed as part of the alkylation reaction and are not impacted by reaction zone mixing. Most of these droplets will likely pass through coalescing media. Effective effluent treating is key to preventing corrosion and fouling of downstream equipment and potential issues with product quality.

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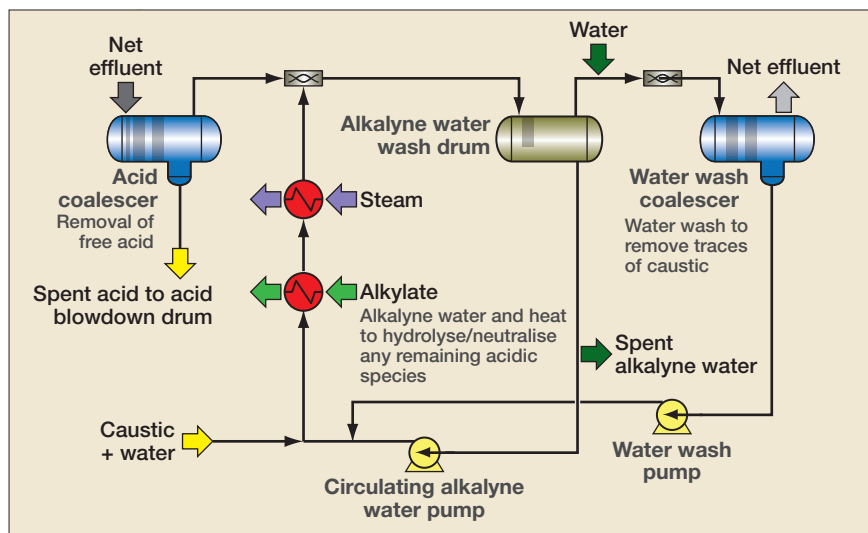


Figure 7 Stratco wet effluent treating system

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Diwakar Rana is the Technology Development Manager for the Stratco alkylation business with DuPont Clean Technologies. He holds a BE in chemical engineering from Deenbandhu Chhotu Ram University of Science and Technology, India, a ME in chemical engineering from Illinois Institute of Technology, a PhD in chemical engineering from Washington State University, and is a licensed professional engineer for the State of Texas.

J Randall Peterson is the Process Technology Manager for Stratco alkylation technology with DuPont Clean Technologies. He holds a BS degree in chemical engineering from the University of Kansas, and master of business administration degree from Rockhurst College.

Rob Ewing is the Innovations and Technology Manager for the alkylation and hydroprocessing businesses with DuPont Clean Technologies. He holds a BS degree in chemical engineering from Kansas State University.