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Raman Spectroscopy

Alkylation

Application Note

An alkylation unit (alky) is one of the conversion processes used in petroleum refineries. It is used to convert isobutane and low molecular weight alkenes (primarily a mixture of propene and butene) into alkylate, a high-octane gasoline component. The process occurs in the presence of an acid, either hydrofluoric acid (HF) or sulfuric acid (H_2SO_4) as catalyst.

Essentially, the alkylation reaction involves circulating the hydrocarbons in a liquid state, achieved by applying sufficient pressure, and maintaining a low temperature alongside a high ratio of isobutane (iC4) to olefin, such as propylene or butylene, from the refinery's fluid catalytic cracking unit (FCC). The reaction mixture then moves to an acid settler, where the acid is recovered and redirected back to the reactor for reuse. Subsequently, the products are fractionated, separating into gaseous LPG, propane, and n-butane, and yielding the valuable alkylate product.

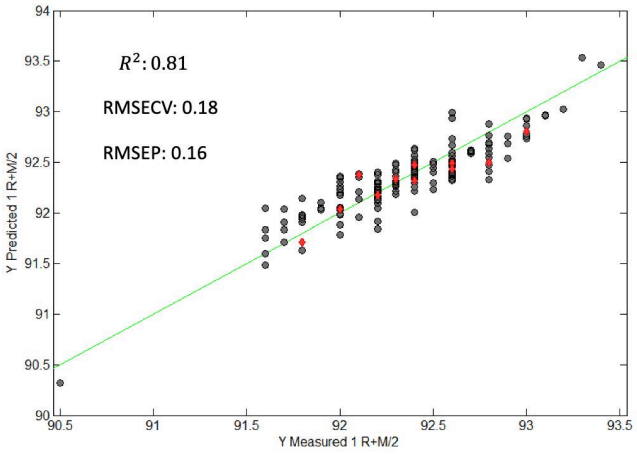

Figure 1: Predicted vs. Measured Alkylate Octane. Measurement obtained using ASTM D2699.

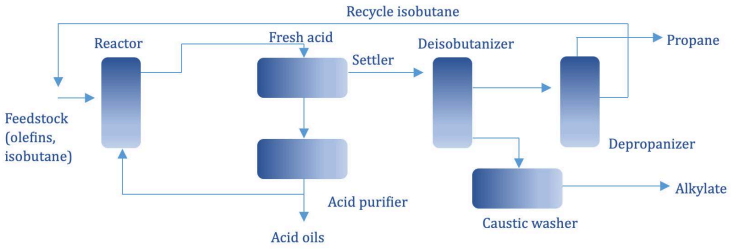

Figure 2: HF Alkylation

Crude oil contains 10-40% of hydrocarbon in the gasoline range. Refineries typically use an FCC to convert high molecular weight hydrocarbons into smaller compounds, which are then converted into gasoline hydrocarbons. The FCC process also creates byproducts of other low molecular weight alkenes and iso-paraffin molecules that are key for this application. Alkylation transforms these byproducts into larger iso-paraffins molecules with a high-octane value.

A key distinction between the two acids is their solubility with isobutane; isobutane exhibits low solubility in H_2SO_4 while showing reasonable solubility in HF, requiring higher isobutane to olefin ratios when H_2SO_4 is used to offset the solubility challenge.

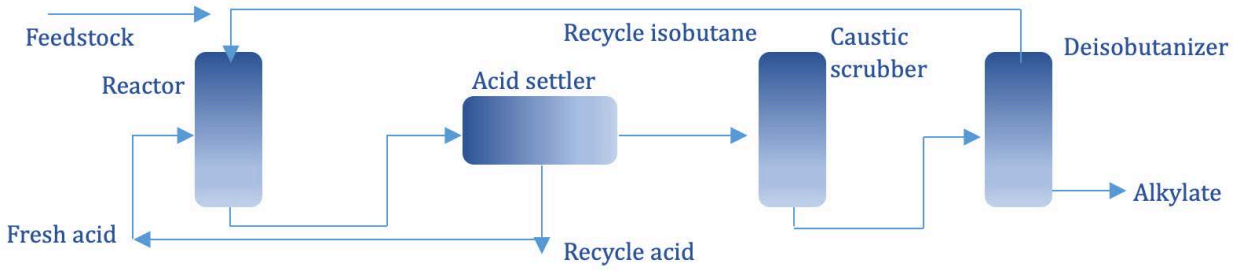

Figure 3: Sulfuric Acid Alkylation

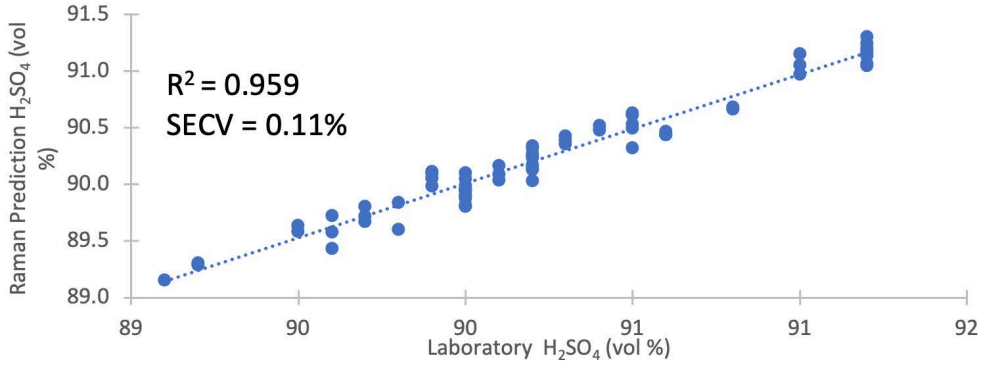

Figure 4: Sulfuric Acid concentration

Alkylation reactions are catalyzed by strong acids taking place more selectively at low temperatures of 70°F for H_2SO_4 and 100°F for HF. The volume of acid used is approximately equal to the volume of liquid hydrocarbon feed. Careful control of the operating conditions produces a high proportion of products that fall in the gasoline boiling range. Operating variables include acid strength, reaction temperature, and isobutane to olefin ratio. The reactions are run at pressures sufficient to keep the hydrocarbons and the acid in the liquid phase. Appropriate mixing of acid with hydrocarbons is essential for high conversions. Furthermore, alkylation reactions are extremely exothermic which requires temperature control during the alkylation process.

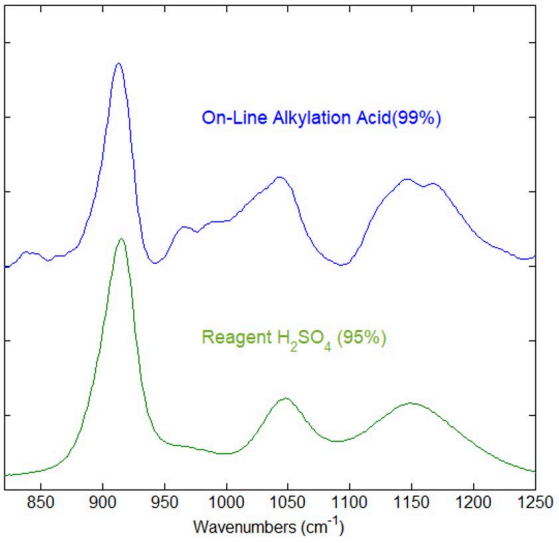

Figure 5: Raman spectra comparing Reagent grade H_2SO_4 & On-Line Alkylation Acid H_2SO_4

PARAMETER	RANGE	r^2	SECV	SAMPLES
PROPANE	0.78 - 9.62	0.998	0.083	126
PROPYLENE	0.46 - 11.57	0.9993	0.08	121
ISOBUTANE	25.76 - 44.164	0.9996	0.105	124
N-BUTANE	8.01 - 15.88	0.998	0.063	125
TRANS2-BUTENE	8.49 - 15.09	0.999	0.06	122
1 BUTENE	3.53 - 11.5	0.9994	0.059	125
ISOBUTYLENE	3.86 - 11.5	0.9996	0.036	126
CIS2-BUTENE	4.63 - 9.18	0.9992	0.035	120
ISOPENTANE	1.19 - 12.32	0.999	0.101	125
N-PENTANE	0.08 - 0.94	0.99	0.028	130
1,3 BUTADIENE	0 - 0.531	0.999	0.0047	125
3 METHYL-1 BUTENE	0.251 - 7.59	0.99996	0.014	129
TRANS2-PENTENE	0.186 - 1.9	0.998	0.023	129
2 METHYL- 2 BUTENE	0.213 - 1.76	0.999	0.016	127
1 PENTENE	0.115 - 0.57	0.991	0.012	127
2 METHYL-1 BUTENE	0.22 - 1.26	0.997	0.015	130
CIS2-PENTENE	0.105 - 0.81	0.994	0.015	126

Table 1: Modeled results showing the resolution of 17 different molecules from a single input stream into an Alkylation unit.

Post-reaction, the mixture exits the reactor and enters a settler, facilitating the separation of the acid and hydrocarbon phases. The separated acid is then extracted and sent back for reuse. The hydrocarbon stream progresses to a deisobutanizer, where an overhead stream composed of propane, isobutane, and traces of HF is directed to a depropanizer. The overhead from the depropanizer stage is channeled to an HF stripper, fractionated (c2/c3) and stored for later use or sold as a pure component.

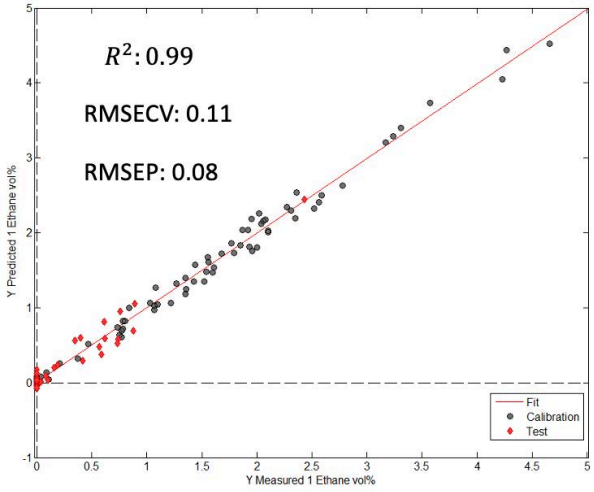

Figure 6: Predicted vs. Measured Ethane. Measurement performed via GC analysis.

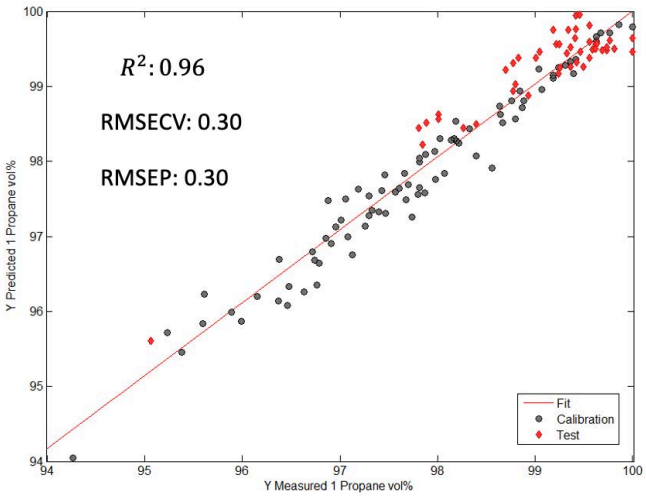

Figure 7: Predicted vs. Measured Propane. Measurement performed via GC analysis.

Isobutane isolated from the deisobutanizer main fractionator is looped back into the system. Finally, the lower stream from the debutanizer, alkylate, is forwarded for inclusion in product blends or sold as is.

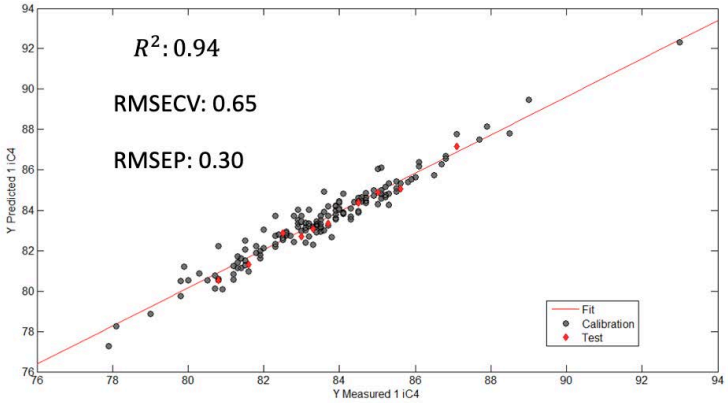

Figure 8: Predicted vs. Measured i-Butane. Measurement performed via GC analysis.

The HORIBA's Process Instruments brand is specifically designed to detect below 100ppm with some compounds in the single digit ppm range. A diode laser is optimized for fiber optics illumination and collection via a flow cell with a sapphire window. Collected radiation is returned to the monochromator with a fiber optics slit which is mated to a diffraction grating and 4-stage cooled CCD camera for detection. The HORIBA Process Instruments design is fast and efficient, with minimum energy loss to maximize detection.

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