Question 73: Does alkylate volume yield decrease if T90 increases? Have you quantified the costs and benefits of reducing T90 by changing reaction conditions?

KAISER (Delek Refining Ltd.) With respect to alkylate yield and T90, the short answer to the question is, yes. When T90 increases, your alkylate yield is going to go down. And if that's all you care about alkylation, you can go to sleep for the next five minutes and Jeff will wake you up when we get done. The two are tied together at the hip by the polymer make. The things that tend to give you heavier alkylate are doing so because the polymer make and the amount of tar in the unit is going up, and it's influencing the T90. It's also taking away from the good quality alkylate that you want. The table below is also in The Answer Book. You see some directional influences for the things that refiners tend to have direct control over inside their unit: iso-to-olefin ratio, acid/hydrocarbon ratio, acid strength, and so on. The first column is in terms of increasing parameter. If you increase your iso-to-olefin ratio, the T90 will tend to come down; the yield will go up; and also, the alkylate octane will go up.

Alkylate Yield & T90	Increasing Parameter	T90	Yield
	Iso/Olefin	?	?
	Acid/Hydrocarbon	?	?
	Acid Strength	?	?
	Iso Recycle Purity	?	?
	C5= and/or C4== Feed Composition	?	?
	Feed Contaminants	?	?
	Reaction Temperature	?	?
	Reaction Time	?	?

We won't spend a lot of time on that slide because it's in the book. You can look at it and reference it in relation to this next slide where we talk about everything that you have a handle on that you can adjust is a range; there's a spectrum. There's an area that you want to try and operate your unit in to give you the best balance between not only yield and T90, but also within equipment constraints and also within safe operating parameters for the different things inside the unit. The table below shows you rough—and I do want to emphasize rough—guidelines that are highly situational dependent. The parameter is in the center; there's a spectrum to the left; and, there's a spectrum to the right, in terms of increase and decrease in parameters. The four items on the top—the iso/olefin ratio, acid/hydrocarbon, the acid strengths, and the isobutane recycle purity: those are the kinds of things that you're going to want to tend to maximize as much as you're able in order to minimize the alkylate T90 or decrease the alkylate T90 and increase your alkylate yield. The things on the bottom are the kinds of things that you're going to want to minimize. You're going to want to have lower feed contaminants. Lower reaction temperatures will tend to decrease the polymer make, decrease your T90, and increase your alkylate yield.

Red	Yellow	Green		Green	Yellow
4	**6**	**8**	**Iso/Olefin**	**14**	**16**

Alkylate Yield & T90 Rough Guidelines - Situational Dependent!

Red	Yellow	Green	
4	**6**	**8**	**Iso/Olefin**
0.9	1	1.5	Acid/Hydrocarb
80	83	86	HF Acid Streng
84	86	88	Sulfuric Acid St
75	80	85	Iso Recycle Pur
		0	C5= Feed Com
		0	C4== Feed Cor
60	70	80	HF Reaction Te
35	40	50	Sulfuric Reactio

Deviations from "center" range lead to increasing problems / constraints

Straying away from the center is not always a bad thing. I think there are certain things, certainly acid strength, that if you go too low on acid strength, you tend to put your unit in danger of corrosion and eating the thing from the inside out. Lower iso/olefin ratios are not favorable. You can actually get it where you have incomplete reactions and continue to have reactions inside the tower in places you don't want it. There are also practical limits. For instance, on the iso/olefin ratio, if you go higher than 18, it's not that the unit is going to encounter operational problems. It's just that you're probably spending too much in terms of utilities, reboiler duties, condenser duties, electricity in pumping the stuff, and it's not really buying you anything. You've reached an upper practical limit for what you're trying to do and you're not really getting any benefit in terms of your alkylate yield. So what your refiner needs to do is to try and understand where he is in this spectrum. I would suspect that a lot of you are probably already in that green zone. Depending on which parameter you have the most control over, you can do small test runs in your unit or small paper studies to see what happens if I increase this parameter because I have some room there, then how much of a response do I get in T90 and alkylate yield and what does it cost me? You can then make your own judgments from there.

ZMICH (UOP LLC) For the alkylation response here, I've drawn from our Technical Service Department expertise. UOP experience suggests that olefin feed composition probably has the greatest effect on T90, especially the amylene content of the feed. Our experience, "our" being UOP, suggests that fixing the feed olefin content and changing the process variables within normal range of operation would not have a strong effect on T90. In the middle of the slide, in general, for a given olefin feed composition, if the T90 increases, the alkylate specific gravity is also going to increase. For an equal weight yield, there is going to be a volumetric yield loss, as Allen was suggesting. If the T90 is increased by decreasing the isobutene/olefin ratio, then the alkylate octane would be expected to decrease and this effect could be significant. Finally, UOP has not quantified the cost and benefits of reducing T90 by changing the reaction condition.

Alkylation?T90

•Olefin(C5=)hasgreatesteffectonT90

•FixingC5=,changing process variables has small influence

?T90?AlkylateSG

Equal Wt. yield ?volume yield

•UOP has not quantified cost?benefits of reducing T90 by changing reaction conditions

RICHARD DOSS (CITGO Petroleum Corporation) I have a question on some of the ranges from this table that's listed here. It's listing 50°F as outside the expected or optimum operating range for a sulfuric acid reaction. I'm used to seeing that number lower. Is there some more recent test data that's saying 50°F is the bottom of that range?

KAISER (Delek Refining Ltd.) I had to make the table, so I had to put down some sort of a number. What I was trying to imply by having that in a green box is that 50°F is likely to be a good temperature for alkylation reaction. That doesn't mean that if you hit 49°F and you're in the yellow zone, all of a sudden you're going to have subpar yield and you have to do everything you can to get it back to 50°F. This is a very broad spectrum; but in terms of trying to present something concise and understandable in a short timeframe, I put these numbers down. They're a range, and it depends on particular pieces of equipment. But specifically, I would say, no. The 50°F is a good alkylation temperature. We tend to run our reactor in the mid-40°Fs to about 50°F. So for us, we're a little bit cooler than that.

J. RANDALL PETERSON (STRATCO-DuPont) We design new units for 45°F and sometimes down to 42°F. Typically, I think Allen is correct: Most units run between 50°F and 60°F, the ones that are running out there, but you do get a little bit better octane at the colder temperatures.

CAMERON McCORD (Chevron Corporation) We have a sulfuric acid plant. One of the two has what we call a rerun column where we split the alkylate into a light avgas alkylate to the, probably, 75°F to 80°F yield. And then, a heavy alkylate comes off the bottom and goes back to the whole alkylate tank. Has anyone gotten experience, either on the panel or in the audience, with trying to find a better disposition with the heavy alkylate from a rerun column other than gasoline, jet, or diesel given the economic times we're in these days? And, what product quality concerns might you expect?

KAISER (Delek Refining Ltd.) We also have a rerun column and what we're not able to split off as light does go to gasoline. We have sufficient jet-treating capacity that we don't find the need to try and push it into jet. My suspicion would be that it might be suitable. And again, it depends a lot on what you're blending it into. It may not serve as a stream by itself, but you might be able to blend it in there, depending on where you are in terms of some of the cold-flow properties and if you're trying to make a Jet-A versus a JP8. And then, I want to clarify briefly, again, on this table, that some of the things on here are not meant to be as strict limits in how they relate directly to the T90 and the alkylate yield. As Randy pointed out, cooler temperatures do tend to favor alkylate octane and yield, but you're also paying for something. That might mean that you're running your refrigeration compressor a lot harder, so there might be some economic penalties towards running closer to that 40°F. And so, this spectrum is not meant to serve as hard-and-fast limits for how you run the unit, but to serve as kind of directionally economic indicators that there are benefits to going lower than the 50°F, lower than the 40°F. But, they come at a cost and you're going to have to understand the difference between that cost and benefit.

HAZLE (NRPA) Are there other panelists that have comments about disposition of heavy alkylate?

J. RANDALL PETERSON (STRATCO-DuPont) Yes, I have a follow-up comment. I didn't load that question with all that I knew on the subject. [laughter] We have indeed tested the jet for the heavy alkylate for suitable of the jet. It's bad on WISM in the jet. I suspect some of the polar molecules following through from the alkylation process. I was hoping someone might have a comment on how to get rid of those bad properties or if there is another disposition for that stream, perhaps a higher value.

HAZLE (NRPA) Did you want to follow up on the WISM?

KAISER (Delek Refining Ltd.) I will try. I don't know how much room you have on your deisobutanizers (DIB) reboiler; but if you're suspecting polar molecules, you might try to run your DIB a lot harder and try to break down a lot of those esters in the reboiler itself.

RICHARD DOSS (CITGO Petroleum Corporation) Another comment on the table that we have up here: For the units that I am aware of personally there, you find that a lot of people are running more to the right side of that table; its economics. Basically, you're pushing capacity; you're trying to get more through the units. You just can't get over to the left side, but it's the right place to be running because it makes the most money.

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