
Question 11: What process or catalyst options are available for shifting yield selectivities from gasoline to distillate while minimizing the impact on light olefin yields? How are the product properties impacted? How does change-out rate impact the viability of the catalyst options?

HEATER (BASF Catalysts)

Undercutting gasoline into light cycle is the first option and is widely employed. It is quick, it is easy, and it gives an immediate impact. Reducing riser temperature and/or cat-to-oil ratios reduces conversion, while using a ZSM-5 additive to regain C3-C4 olefins is another option.

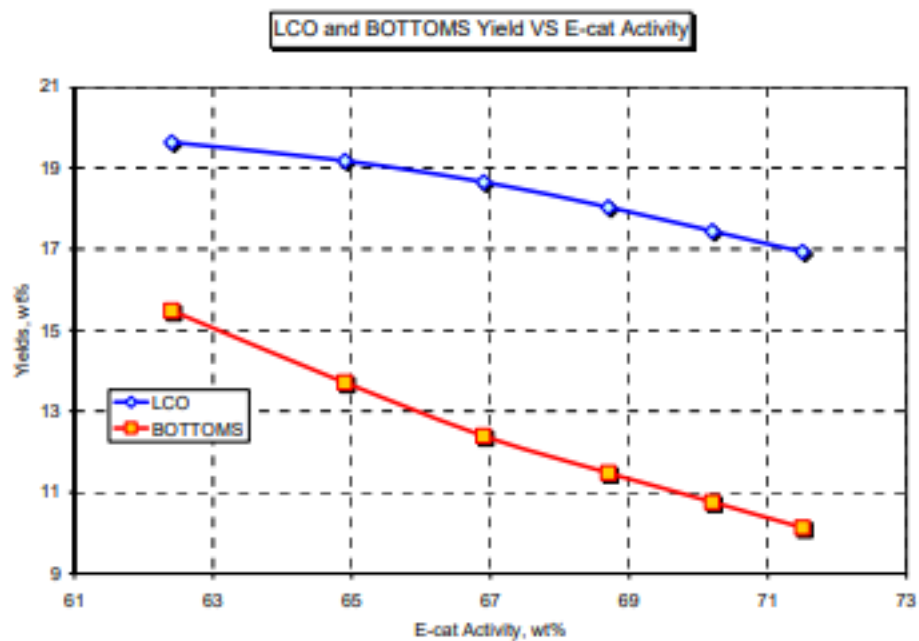
Change-out is always an issue, particularly when the unit has a large inventory. When change-out is being done to take advantage of a small window of opportunity, consider using an accelerated change-out schedule with purchased e-cat of similar properties and technology.

Undercutting gasoline is a flexible option. As I mentioned, it is already commonly practiced, in addition to reduced conversion via lower riser temperature, and/or lower catalyst activity. Unfortunately, the bottom yield tends to increase faster than LCO as conversion is reduced, and I will have some charts in a minute to show that. You can use a heavier feed, but coke, gas, and product quality constraints may limit, for example, the wt% sulfur of some of your products.

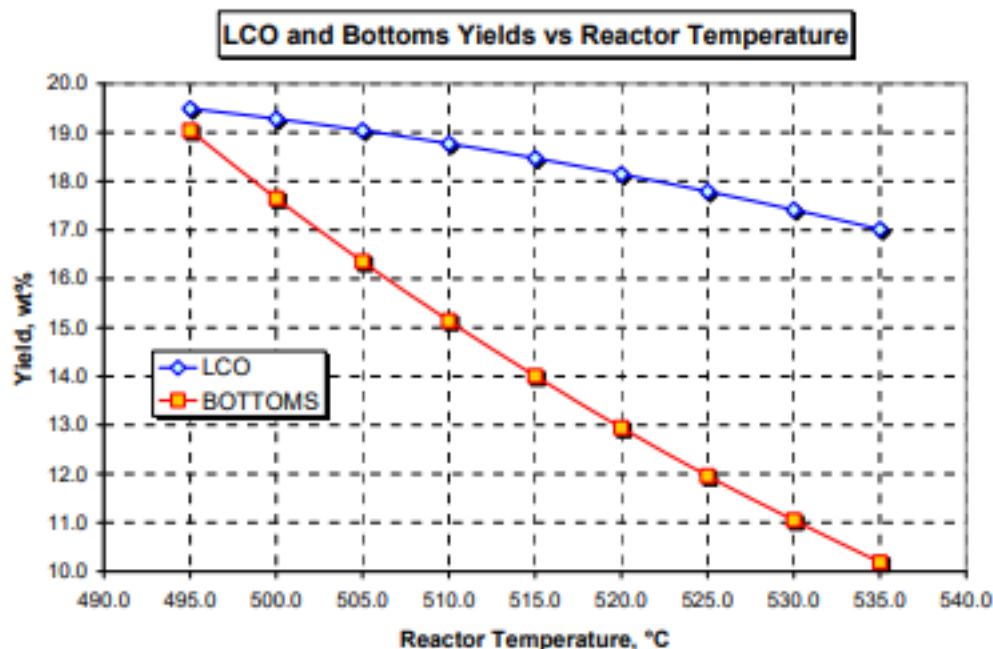
With slurry or heavy cycle recycles, second pass yields are very non-selective. High coke and gas yield tend to be the result, with lower quality LCO that will typically require higher air rate or a lower feed rate to heat balance. And when you go to a lower feed rate, it may end up reducing your net LCO production.

Catalytic requirements for maximum distillate: Increased Lewis acidity versus Bronsted acidity decreases the zeolite-to-matrix ratio, which will increase LCO production and give you better bottoms-up grading capability than you get by dropping riser temperature only. In a minute, I will show a slide to demonstrate that. You need a catalyst with good coke selectivity by selecting the right pore architecture. BASF has commercialized products designed for distillate maximization and continues to work in that area.

This is a chart of light cycle and bottoms yield versus e-cat activity. You can see that as you decrease activity—that is, go to the left on the X-axis—slurry yield increases slightly faster than does LCO yield.



The next slide is LCO and bottoms yield versus reactor temperature.



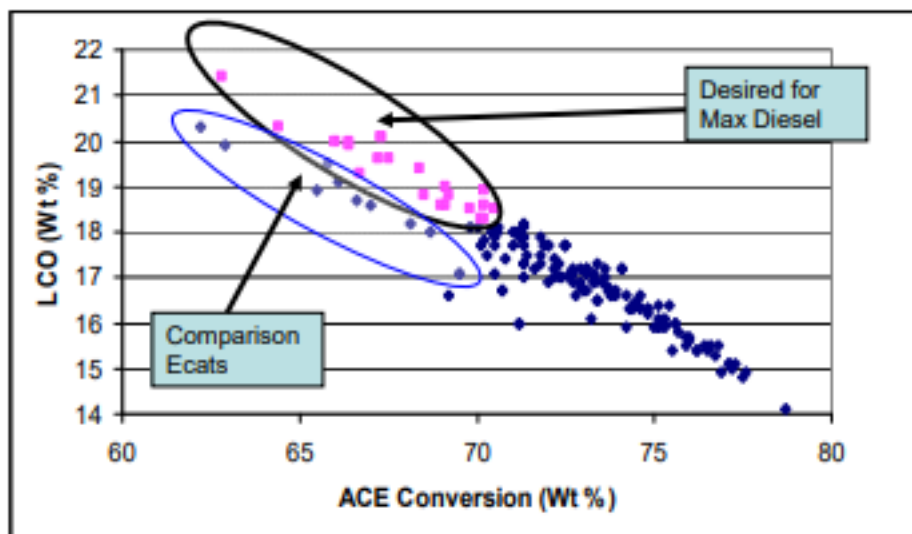
I apologize to my American colleagues for the degree C, but here you see a decrease in riser temperature, once again, going to the left on the X-axis, which gives a much larger increase in slurry than does LCO. So that is generally not the best option.

The point of this slide is to show that there is a difference in catalyst. This is data from our e-cat data-benchmarking database. There is a difference in catalyst when you are looking at LCO yield at a given conversion. Your selection of catalyst can impact that, so you definitely want to talk to your catalyst supplier and see what they can do for you in the area of distillate maximization, if that is important to you.



NPRA

Ecat Benchmarking Useful for Investigating Maximum Diesel Operation



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FCC Q&A

THOMPSON (Chevron)

I agree with the previous comments about undercutting gasoline. That is certainly an option. Cat-to-oil reduction is also another processing option. As far as the catalytic options, bottoms cracking additives are a quick way to get increased LCO. You can also use ZSM-5 to basically make light olefins at the expense of gasoline. The problem there is that you have to make some other moves on the unit. That does not give you more LCO by itself.

The other thing you can work with is zeolite content, as we have mentioned earlier. Zeolite rare earth is another way to handle it, particularly for those who want to make higher quality LCO, since if you reduce rare earth, you are going to minimize hydrogen transfer, which is helpful.

One final comment is that there is not much potential for making distillate when you are processing very paraffinic or highly hydrotreated feeds. Conversion tends to be very high and gasoline is favored over distillates.

WARDINSKY (ConocoPhillips)

As we pushed FCC rates in this industry, one of the things that we have seen is that the diesel range material in your feed typically can be 15% to 20%. And if you think you are going to be in a distillate market for a long time, it is diesel range of material that you are downgrading to LCO, if distillate is valued over gasoline. So you may want to look at upstream projects to get that diesel range material out of your fresh feed. The other thing that we have seen people do is start installing slurry vacuum strippers to try to recover LCO out of the slurry.

One thing I wanted to elaborate on a little bit is severely hydrotreated feedstocks. We have moved a couple of our units to that type of operation and we believe that distillate mode may be limited with that kind of operation, because first of all, there are fewer LCO precursors in the feed following severe hydrotreating. You are also going to want to retain high e-cat activity and high riser severity to keep your regenerator dense bed temperature up.

Finally, in order to maintain level in the bottom main fractionator, we have seen those operations move to try to maximize heat recovery from the HCO and slurry pumparounds. So you are effectively dropping LCO material down into the bottom of the fractionator and losing it there. If you move to that kind of operation, be aware of what the pitfalls may be.

SHANKAR VAIDYAHATHAN (Fluor Corporation)

My question is regarding the heavily hydrotreated feed. Is it 1,000 ppm sulfur severely hydrotreated feed that affects the selectivity to diesel products? Or, at what severity do you begin to affect the selectivity of diesel range material?

WARDINSKY (ConocoPhillips)

We have a couple of units that run with 150 ppm feed sulfur. It is a 2,000 psia hydrotreater. It is putting in about 1,000 SCFB of hydrogen. The light cycle yield is only in the range of, say, 7% to 8%. They are running a 90 to 92 conversion.

THOMPSON (Chevron)

We have a similar operation at one of our units. They make ULSD off of the feed hydrotreater.

KEVIN PROOPS (Solomon Associates)

I would like to thank Mike for his comment. I was going to say largely the same thing; that the FCC is a gasoline-making machine. If this question was motivated by the high diesel prices in 2005 and 2006, the right answer is to get the barrel out of the cat cracker in the first place. Pete Andrews asked me to say

that, by the way. [laughter]

If you have a scorecard that says you want to reward your refinery FCC people for keeping the FCC full and keep going on your same project, Mike mentioned to go get some of the gas oils out of the bottoms and put that in the FCC instead. It is the crude vacuum unit sometimes, and it is also coker gas oils in the gas oil hydrotreater. At the refineries where I have worked, we have seen that there is a lot of the diesel in the coker gas oil as well, and that is certainly fertile ground to go chase.

The comment in the question that asks about minimizing impact on LPG yield: In the past, I have seen that distillate tends to make a fair amount of LPG. So if the questioner is asking about maintaining yield, that is easy: That is overcrack. Or just put some ZSM-5 in if you have to, so that should not be an issue. I think the right answer is to keep the distillate out of the FCC when you can.

HEATER (BASF Catalysts)

No.

DOC KIRCHGESSNER (W.R. Grace Refining Technologies)

We have commercialized a catalyst system that we call Genesis and reported on it in our most recent catalogram, which has been issued for this meeting. In it, we discuss the success of this type of technology, particularly for upgrading bottoms into LCO without running into coke selectivity disadvantages. In terms of shifting economics, I think Mike pointed out, or Kevin said, that cat crackers are primarily gasoline machines. But as economic changes require a shift towards higher value for diesel, we find that it is easy to adjust the formulation of these catalysts, both for activity and for upgrade into LCO.

RAY FLETCHER (Albemarle Catalysts)

It might be interesting to let the audience know that Albemarle Catalysts has spent a substantial amount of research on this question of shifting gasoline into diesel. And, as we all know, the FCC is an asset that is designed genuinely for making gasoline. We have a catalyst that is now in the scaling-up process. We gave a presentation in Athens earlier this year, in timing with our patents going public. The catalyst is designed to make the FCC a max diesel engine. This catalyst is capable of increasing the diesel yield by 20% to 25% volume relative. But, at the same time, it reduces the LCO aromatics by 40% to 45% absolute. And if you use just a simple rule of thumb that equates aromaticity to cetane number, which is basically taking the delta in LCO aromatics and multiplying it by 0.6, you get an approximation of what the cetane improvement would be. This would give us an improvement of about 25 cetane number.

This material has been produced on a small scale. We have put it into a small heat-balanced unit running about 200 liters a day, and it produced the same yield selectivities as in our laboratory work.

Again, this material is in scale-up. It probably will not be available for sale at least until next year, probably towards the end of next year, but there is light at the end of the tunnel for those refiners who wish to shift their FCC from a gasoline engine to a diesel engine.

ED PALMER (Mustang Engineering)

I had a question for the commercial experience for the severely hydrotreated cat feed, the LCO. By property, as far as gravity, is it still less than 20 and still around 50% to 60% aromatics?

THOMPSON (Chevron)

Yes. I would agree with that because those operations tend to run higher severity. It depends, in part, on your catalyst. If you are running a high activity, high matrix catalyst, you are going to get a lot of hydrogen transfer; and that is going to basically pull hydrogen out of the LCO and into the gasoline. So you can change your catalyst formulation. You can go to a low hydrogen transfer catalyst and help that a bit; but generally, the LCO quality is not nearly what you would expect for good quality diesel.

WARDINSKY (ConocoPhillips)

Gravity is at about the same range as it was prior to the feed shift. I do not know the answer to the aromatics question, whether the aromatics content has changed or not.

JIM WEITH (Mustang Engineering)

You mentioned the vacuum flasher on slurry. I did advise at a refinery in Wyoming where they had this. It was a tower that was hooked onto the side of a vacuum tower. They ran the slurry through it, and reportedly, that was going to pull the distillate out of the slurry and put it into the light cycle or into the light vacuum gas oil that then went off to a hydrofeeder and out somewhere. The vortex meters on it were too big at the time, so we really could not get a real good material balance on it; and I left before those got replaced. It did look like it was doing some benefit. And being close to Halloween, it might be a note that this was called the slurry flasher. But if you listened to people in heated conversations, it got slurred a little bit into becoming the furry slasher.

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