



Webinar – FCC Slowdown & Unit Optimisation during Global Pandemic (Q&A)

Q 01. How does FCC fit in the Oil-to-Chemical concept being pursued currently in the middle east, giving that most of its crude oil are heavy? Does the shale oil represent a better feed?

A 01. The main role for FCC is in supply of PC intermediates – such as light olefins, especially propylene. ZSM-5 additives are often used to maximize the production of FCC propylene that is used in the production of polypropylene. Additives such as ZSM-5 are proven technologies will all types of FCC feed.

Shale oils are generally very light and tend to produce less coke. Heavier feed should therefore be better for the FCC during turn-down because the FCC needs to produce coke to maintain sufficient regenerator temperature at a consistent high catalyst circulation rate. Also, many shale oils contain high levels of contaminate iron that can poison the main catalyst. Shale oil is unlikely to play a significant role considering the large quantity of lower production cost conventional crudes available in the region.

If, for economical reasons, a Resid FCC moves to lighter feed such as shale oil, there is a high chance that the heat balance will be deficient due to lower coke burning, and as a result, regenerator temperature may be too low. In this case, some mitigation actions can be taken, for example HCO (or even slurry oil) recycle. In many refineries, the HCO product has a low value. Hence HCO recycle is common practice to produce coke and help the heat balance in FCC units processing light feeds. This can also help to maximize conversion to LCO in FCC units operating in distillate mode with lower reactor severity and high ZSM-5 usage, as many refineries have been doing recently.

The HCO can be recycled back to the riser at various locations depending on the FCC unit design:

- At the main feed injection location through dedicated feed nozzle(s):
 - Avoids risk of eroding main feed nozzles
- Mixed with fresh feed and injected through the main feed nozzles:

- Fairly common practice with HCO, but also considered possible with slurry where latest erosion resistant feed nozzle designs as slurry solids diluted by main feed
 - Injected through dedicated nozzles located > 3 m downstream of the main feed:
 - the quenching effect raises the temperature below the mix zone at constant riser outlet temperature which improves feed vaporization.
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Q 02. Do you suggest a book/papers that I can read to further understand FCC on depth?

A 02. JM offer many detailed papers referring to FCC Additive related topics. For general FCC knowledge, the following two books are good references:

- "Fluid Catalytic Cracking" by Reza Sadeghbeigi.
 - "Fluid Catalytic Cracking – Technology and Operation" by Joseph W. Wilson.
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Q 03. In some regions, gasoline price and demand has rebounded with easing government restrictions. What ways are there to quickly switch between gasoline and diesel mode?

A 03. Where gasoline margin has recovered, customers can quickly recover conversion by increasing reactor temperature and where possible reducing feed preheat temperature to increase Cat/Oil. These are quick operating handles to increase conversion. Reducing feed preheat temperature should be within normal operating experience and within guidance provided by the feed nozzle licensor. Other ways to increase Cat/Oil include re-optimising stripper performance.

ECAT activity can also be adjusted to increase conversion. However, this response will be slower. Johnson Matthey offers a HI-Y additive which can quickly increase Z/M ratio of the ECAT, allowing the refiner to quickly adjust yields without the negative impact of increased thermal cracking via increased reactor temperature.



A multiple FCC additives approach is a key strategy to quickly switch between Gasoline and Diesel mode. The circulating inventory can be considered as a true independent variable of the FCC unit. While the base FCC catalyst usually requires tremendous inertia to change (lengthy catalyst selection procedure, long time to change out fresh catalyst hopper and circulating inventory, etc.), FCC additives provide an “on/off” switch to take advantage of transient market shifts.

Current State of the Art for real time optimization is to use an INTERCAT_{JM} multi-compartment addition systems, in combination with our additives:

- HI-Y (to boost conversion when switching to Gasoline mode)
- BCA (to upgrade Bottoms with maximum LCO when switching to Diesel mode)
- SUPER-Z (to maintain LPG olefins production constant in both Gasoline and Diesel modes)

Q 04. At what concentration level will ZSM-5 stop increasing LPG olefin yield?

A 04. Peak ZSM-5 activity varies from unit to unit & is be impacted by a number of things (e.g. the main catalyst formulation, especially rare earth level and subsequent level of hydrogen transfer; the unit configuration; and the type of additive you are using). In conventional FCC units the LPG production plateaus at about 10-15% ZSM-5 crystal in inventory and the typical max propylene yields are in the region of 10.5-11wt%_{FF}.

A key limiting factor for max light olefins production is the rate of the reverse oligomerization reactions. The forward beta-scission cracking reactions occurring on the ZSM-5 active sites will ‘complete’ with the reverse C3 + C4 olefin oligomerization reactions, and ultimately reach a thermodynamic equilibrium. Reducing the HC partial pressure in the riser helps to drive the equilibrium to form more light olefins (Le Chatelier’s principle). But for most, there is diminishing returns above about 15% ZSM-5 crystal in the inventory.



Q 05. What limits the minimum regenerator temperature?

A 05. The minimum limit on regenerator temperature is quite complex and is unit specific. Most regenerators should continue to have successful coke burn at temperatures as low as 680°C. However, as the regenerator temperature is lowered below this, coke burning kinetics slow down and there is increased risk of not being able to fully regenerate the catalyst. ECAT properties must be monitored, and a visual check can be made to identify changes in catalyst colour: darkening through grey to black is indicative of higher carbon on regenerated catalyst (CRC).

As regenerator temperatures cool, catalyst circulation rate (CCR) increases to maintain reactor temperature. The risks associated with high CCR are that the unit may be operating close to the slide valve dP trip settings.

As a consequence of the slower coke burning kinetics in a full burn regenerator CO may break through from the dense bed causing afterburning in the dilute phase where there is little catalyst present to absorb heat of combustion. Afterburning often limits throughput or operational flexibility and eventually, can result in serious damage to internals leading to premature shutdown & costly repairs. Note that increases in afterburning may also be caused by maldistribution from lower air rates at reduced unit throughputs. To protect your FCC from regen afterburning, JM provides a wide range of CO Promoters Platinum based or non-Platinum based (for NO_x sensitive units). Kinetically limited operations generally respond very well to CO Promoter use.

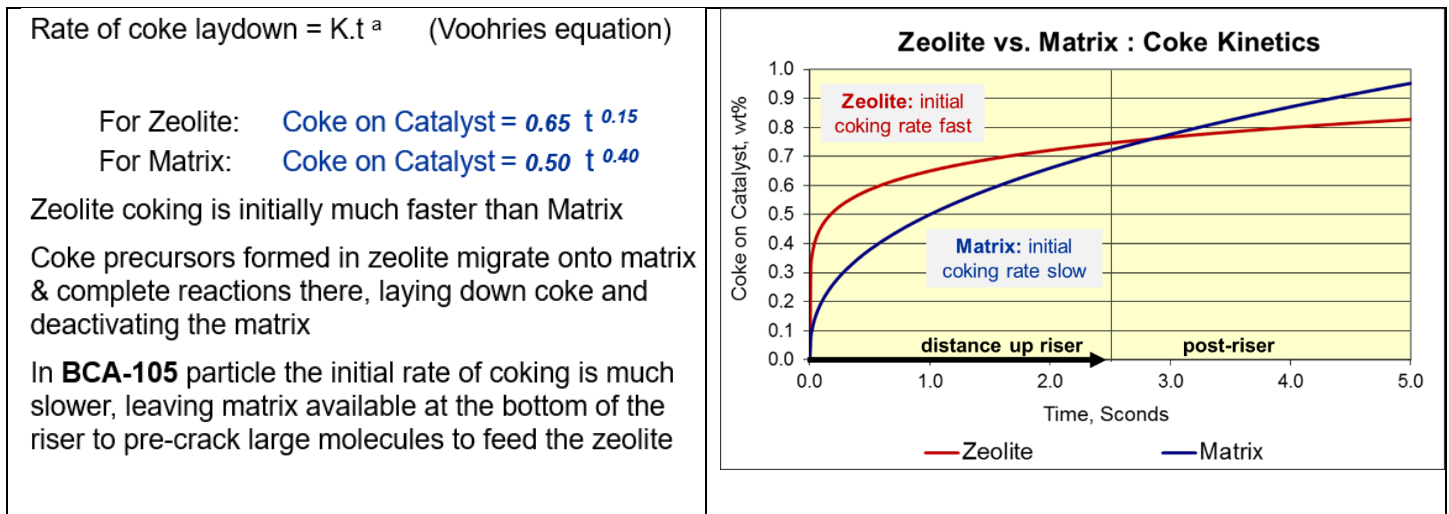
Q 06. I'm struggling with low regen temperature at low feed rates. We've stopped O2 enrichment since we are at reduced rates. Will re-introducing O2 enrichment help to manage our low regen temperature?

A 06. Oxygen enrichment can be used to maintain constant xs O₂ at lower air rate. Lower air flow means there will be a higher partial pressure of O₂ and less nitrogen going to the regenerator. Nitrogen essentially gets a free pass through the regen and acts like a heat sink. Therefore, minimising N₂ in air (by enriching oxygen) will have a positive impact by directionally increasing the regenerator bed temperature.

Nonetheless, the air flows must not be reduced so much that the cyclone efficiencies are compromised, as you may incur increased catalyst entrainment with the flue gases. Also, if there is maldistribution in the regenerator caused by low air rates, then less air might make things worse. In most cases, O2 enrichment should help, but it does depend on what exactly is going on in your regenerator.

Q 07. Besides the ability to change the Z/M ratio of the catalyst inventory more quickly are there additional advantages of using a Bottoms Cracking Additive vs. simply increasing the base catalyst matrix content?

A 07. Adjusting Z/M ratio using a separate particle additive which does not contain zeolite has a positive effect on coke kinetics. Catalytic coke follows Voohries equation which has the form:



Q 08. What is the maximum acceptable chlorides content in FCC Feed?

A 08. This number can change and is dependent on how the fractionator is operated. If the amount of chloride in the FCC feed is known, then the salt deposition temperature can be calculated. Once this temperature is known, the fractionator must be maintained ~10 deg F above the temperature to ensure chloride salts are not formed in the tower. It is also important to have good desalting at the crude unit, and if chlorides will always be high consider installing an FCC feed desalter.

Imported feed should be properly water drawn before being placed on feed which will help minimise any chlorides. We have also seen a limit of 3 ppm total chloride used as a benchmark for import feeds. However, it would be good practice to work out the HCl and NH₃ partial pressures based upon 5 ppm chloride and determine whether the NH₄Cl dissociation constant is above or below the equilibrium line at given operating temperatures of the main fractionator. This will then provide an indication of whether a 5 ppm limit on feed is acceptable.

Temperature becomes a key factor where "any" level of chlorides are present. Below the dew point of ammonium chloride you will get deposition and accumulation. Typically, 112 degC or lower is prone to salt deposition – so operations pushing naphtha overhead are much less susceptible to fouling. However, you must also consider the pump around where cold naphtha is fed into the top of the main fractionator causing local quenching – which may make a "cold spot".

As a cross check, it would be good to understand the condition of the trays in the top of the fractionator. If they are all pitted, it is likely that ammonium chloride corrosion occurred and has caused under deposit corrosion > NH₄Cl would be removed during steaming of the column but we would expect corrosion by-products to be remaining on the tray.

Q 09. From a FCC catalyst perspective, would you be able to comment on 10 ppm chloride in feed?

A 09. 10 ppm Cl in feed is quite a lot and certainly a red flag. There is generally an excess ammonia present, so the amount of ammonium chloride is determined by the chloride level. You can run the maths



- 10 ppm Cl in the RX is $10 \times 53.5/35.5 = 15$ kg NH₄Cl per 1000 MT feed - how much salt does it take to foul the main frac?

Cl is not recognized as being a bad poison for the FCC catalyst because it should never form HCl in the FCC below its dew point. However, feed Cl is usually due to NaCl so perhaps a bigger problem for the catalyst is the associated sodium ($23/35.5 = 6.5$ ppm Na per 10 ppm Cl). Typically feed metals concentrate up by a factor of $\sim 1,000$ ["Added" ECat Na (ppmw) = Feed Na (ppmw) x Feed Rate (MT/d) / CAR (MT/d)] - so 6.5 ppm feed Na equilibrates to $\sim 6,500$ ppmw or 0.65 wt% on ECat - which is a LOT of Na. Na problems begin with as little as 0.1-0.2 wt% added Na on ECat.

Q 10. Having a water purge configuration in main fractionator what is the maximum chlorides in feed we can deal with? Are values over 10ppmw in the feed acceptable?

A 10. There are several things we typically consider:

- 1) Effect of Cl on equipment and corrosion
- 2) Effect of Cl on metals on Ecat
- 3) Risk of ammonium chloride salt sublimation in the main fractionator
- 4) Impact on water wash operation

Q 11. Do you have customers facing increased coke formation in vapor line?

A 11. Our global technical service team is working with many FCC units around the world. Unfortunately, we do have some customers reporting transfer line coke formation. E.g. a customer in Europe recently had a lot of coke fall off and arrive in the main fractionator when they shut down the FCC unit.

Coking in the vapour line is a common problem, especially when processing heavier feedstock. It usually occurs in stagnant zones (e.g. the insides of bends in the transfer line where the velocity will be lower) or cold spots. Key areas where cold spots are found are the big blind flange at the inlet to the main fractionator which is occasionally insufficiently insulated due to safety concerns.

Another common area is shortly after the inlet flange at the point where the product gases enter the main fractionator. It is important that the tray design immediately above the main column inlet nozzle are designed to direct the down-coming liquid away from the product gas inlet. We have seen a shroud/hood installed above the inlet nozzle to direct the liquid away from this area and refractory lining to thermally insulate the inlet nozzle from the inside.

Coking can be detected by closely monitoring the transfer line dP and seeing whether it is increasing over time. If the rate of increase in dP becomes greater when using specific types of feed, then this should be a red flag that these feedstocks are increasing the rate of coking.

When processing heavier feed, especially in distillate mode operation, it is important to keep an eye on the dew point of the feed and ensuring there is sufficient ROT to overcome this dew point. The dewpoint at the mix zone can be calculated from the feed density and distillation, the amount of dispersion steam and the pressure at the point of injection. You should always aim for the mix zone temperature to be above the calculated dew point and this is done by adjusting the ROT. And you can assume the temperature reduction between the mix zone and the riser top (due to the heat of cracking) to be 35DegC.

At reduced throughputs the velocity of the product gases through the transfer line will be reduced and can be supplemented with additional steam added to the base of the riser. This will additionally help to ensure the reactor cyclone velocities are sufficient to ensure good catalyst separation and minimise slurry fines.



Q 12. Addition of ZSM5 produces both C3 and C4 olefins from gasoline range material. If the C4 olefins are fed to an alkylation plant, it will be combined with iC4 to produce alkylate. So what is the true net reduction of gasoline product?

A 12. Lots of customers right now are talking to us about how to run the FCC at low feed rate and how to run the FCC in combination with the alkylation unit. It is a real mix, some people want to continue to make lots of alkylate, while there are other refineries who are shutting down the alkylation unit.

The following numbers can be used as a rule of thumb to estimate how much of the incremental delta LPG yields are converted into alkylate:

$C3= + 1.37 iC4 \Rightarrow 1.8 \text{ Alkylate} + 0.1 C3$

$C4= + 1.12 iC4 \Rightarrow 1.76 \text{ Alkylate}$

Therefore, it really depends what is being sent to the alkylation unit. If only C4= is alkylated, then the net gasoline (Cat naphtha + Alkylate) volume change with ZSM-5 should be negative. If both C3= and C4= are alkylated, the net gasoline volume change with ZSM-5 is positive.

Q 13. I'd like to ask you more about my FCC how do I get in touch?

A 13. Probably the easiest route is to get in touch with Jennifer Rennick, you would have each received correspondence from her with your registration confirmation and login details. She will be able to direct you to the appropriate person(s).



Q 14. I want to increase my ZSM-5 concentration from 2 to 4%. Can I extrapolate the yield shifts? And will I see any dilution effect?

A 14. At these levels of ZSM-5 in inventory the incremental yield shifts are almost linear with increasing concentration, so extrapolating the delta shifts should be reasonably close to actual. However, we would be more than happy to run our model for you and give you more accurate projections.

At these low levels you will not see any dilution effects. We have customers using as high as 25-30% additive and do not experience significant activity dilution of the main catalyst activity. However, dilution can have a positive side: units using very high levels of ZSM-5 do see lower hydrogen transfer, which leads to increased preservation of the olefins formed.

Q 15. How low [temperature] can you safely operate your regenerator?

A 15. This is highly dependent on the coke burning kinetics and unit heat balance. If the regenerator temperature is taken too low you may be limited by the slide valve dP trip SP. CO Promoters can help to bring the coke burn into the dense phase that will help, and some units will have operating levers such as Catalyst Coolers to help manipulate the regenerator temp. It is also possible to deoptimize the stripper by reducing the stripping steam ratio, and some refiners may opt to fire the DFAH or torch oil guns.

Q 16. Please go over the ways to increase distillate

A 16. Refer to slides in Webinar slide deck. Key ways to maximise distillate include:

- Reduce ROT
- Increase feed preheat
- Reduce ECat activity



- Undercut gasoline
- Overcrack gasoline
- Recycle HCO / Slurry
- Reformulate catalyst to increase MSA (slow)
- Use Bottoms Cracking Additive to increase MSA (fast)

Q 17. Can you send me information about loaders? Would we need to buy one?

A 17. Of course, we can get in touch directly and discuss what loader options we have. Usually when a customer is using one or more of our products then we can supply one of our loaders free of charge under a lease basis. We have more than 290 loaders in the field at the moment and customers find them the most reliable way to load both fresh catalyst and additives. For general information about our loaders you can also visit our website:

<https://matthey.com/en/products-and-services/chemical-processes/additives/addition-systems-1>

Q 18. What limits the amount of ZSM-5 you can use?

A 18. Typically, the limit is set by the amount of LPG you want to make and how effective the ZSM-5 is at producing LPG at maximum concentrations. Often gas plant handling capabilities limit the amount of LPG you can make, but assuming you have room on the gas plant, then the main limiting factor is the reverse reactions occurring in the riser. Light olefin oligomerization competes with the gasoline olefin cracking reactions enhanced by ZSM-5. The greater amount of C3 and C4 olefins, the greater the driving force for the reverse reactions. Reducing HC partial pressure in the riser can help drive the equilibrium in favour of C3 and C4 olefins, but there is no way to completely stop the olefin oligomerisation reactions from taking place. You will reach a point, usually at about 15% ZSM-5 crystal in the inventory in a conventional FCC, where any additional ZSM-5 will not make any difference to the yields. The yields will naturally reach a thermodynamic equilibrium which is independent of any additional Mobile 5 Zeolite.



Q 19. I am interested in HI-Y, can you tell me more about it?

A 19. HI-Y™ is a high activity Zeolite additive which can be used to quickly increase Z/M ratio. Therefore, it is very effective way to switch back into gasoline mode operation if you have been using BCA to maximise the distillate. Increasing catalyst zeolite activity is a selective way to maximise gasoline. Increasing riser temperature will also increase gasoline via increased conversion (up to the over-cracking temperature) but it will additionally increase LPG and dry gas. Above the over-cracking temperature, gasoline is being cracked into LPG.

Customers have also used HI-Y to recover from a Na metals poisoning, a recent example was a customer in Asia who found it to be a very effective way to quickly recover zeolite activity. However, if metals poisoning is due to vanadium or iron, we recommend our **CAT-AID™** additive which has the ability to immobilise vanadium and reverse the impact iron has on the surface morphology of the catalyst. But in terms of maximising gasoline quickly, other than using operating levers on the FCC, HI-Y is a very effective solution.

Q 20. What is more convenient to use in a FCC unit, an integrated formulation with ZSM-5 or separated additives for octane and SOx?

A 20. Separate additions of all additives allows for maximum flexibility, which is highly important when operating strategies are volatile. ZSM-5 and SOx requirements are independent of each other and also independent of base catalyst requirements (e.g. adjusting the base catalyst for constant metals levels is often not consistent with ZSM-5 or SOx requirements).

However, we do have a few customers that have limitations leading to only being able to add a single additive product. In this case it is possible to prepare pre-mixed combinations of additives together, but this is not the preferred practice because of the limitations in flexibility it brings.



Q 21. Is it realistic to think that an HS-FCC unit will ever be built in NA for 20 wt% C3= production?

A 21. The USA is traditionally a gasoline market, and the economics of cracking gasoline to propylene is generally under pressure from demand for high octane gasoline. Therefore, propylene prices have historically been well below the other higher value products (gasoline, diesel, even butylene which typically is processed into alkylate/gasoline). Furthermore, there are a number of PDH projects moving ahead in NA which may make the economic attraction of an HS-FCC a little less attractive.

There also does not appear to be any shortage of propylene or upcoming increased demand that would cause a spike in propylene values. As long as the propylene value remains relatively low, there does not appear to be a push towards high PP production FCCs in NA. Gasoline and diesel remain king.

Q 22. If I am close to a coke burning limit, will BCA addition increase coke formation?

A 22. The use of BCA does not generally increase coke formation in short contact time FCC units. BCA actually slightly improves coke selectivity, or at worse, coke remains neutral (see Q 07).

Normally, coke precursors formed in zeolite can migrate onto matrix active sites and complete reactions there, laying down coke and deactivating the matrix activity. As BCA-105 is a separate particle, the risk of coke migration is minimized. The rate of coking on Matrix is slower than it is for Zeolite Y as the acid sites are weaker. Therefore, by having a separate particle with a high MSA, matrix activity is retained much longer and allows improved matrix activity at the bottom of the riser.



Q 23. The global pandemic seemed to hit China first, has China started to recover

A 23. China is the 2nd largest oil consumer in the world and we have seen a robust recovery/rebound in China (the demand is close to the pre COVID demand). This is reflected in steady growth in oil prices since early May. We are also seeing good recovery from the 3rd and 4th largest oil consumers in the world, India and Japan.

Secondly, we have started to observe recovery of investment in the industry in Asia with the announcement of the revival of a new refinery build in China. This really is a welcome sign for the Asian market and of course this also gives us an optimistic view for the global economy as well.

Q 24. What is the lowest Reactor Pressure (ignoring Wet Gas Compressor) recommended to maximise Propylene?

A 24. See answers to Q 04 & Q 18. Minimizing HC partial pressure will increase propylene yield. The lowest possible operating pressure is recommended.

Q 25. What is the lowest sustainable Regen Temperature you have observed?

A 25. JM has observed Regen Temperature as low as 1220 F, 660°C. Excess O₂ was very high (over 10%). Most regenerators are better served at operating above 680°C. Please remember these operating parameters and unit and feed specific.



Q 26. Have JM evaluated separate ZSM-5 compared to ZSM-5 integrated catalyst performance?

A 26. There are many benefits of using ZSM-5 as a separate particle as opposed to integration into the catalyst system. When economics change it is important to be able to change with them. ZSM-5 as a separate particle can be very quickly baseloaded to start achieving LPG yield increases. The concentration can also be increased or decreased to get more, or less, LPG. If a unit goes down and there is room on the alkylation unit, ZSM-5 can quickly fill the void. In turn, if economics change again, ZSM-5 can be removed from the unit immediately and yields will decay over a few weeks. Having ZSM-5 integrated into the catalyst system decreases flexibility significantly and does not allow the refiner to capitalize on shorter economic opportunities.

Q 27. Do you see a spike in ZSM 5 in recent event? Do you foresee hitting production limit on your end? and impact on ZSM 5 pricing?

A 27. JM has seen a fairly significant increase in ZSM-5 demand due to Covid-19. At this time the demand seems to have stabilized and we do not expect to have any issues meeting the required demand at current levels.

Q 28. At what minimum ROT, FCC could operate to have minimum coking in reactor vapor line to Main fractionator?

A 28. Reactor vapor line coking is unit and feed dependent. JM has seen units run with ROT as low as 920°F or 493°C without significant issues. These low temperatures were achievable due to the particular FCC's feed composition. Reactor vapor line coking is normally due premature condensation of the heavy products which then experience thermal cracking to produce coke. The lower the ROT is operated the more likely this will occur. The pressure drop from the Reactor Outlet to the Main Column inlet should be monitored and trended daily.



The minimum temperature is determined by calculating the dew point at the feed injection zone. (See answer to Q 11).

Q 29. Does ZSM-5 additive only cracks gasoline range fractions from FCC or other refinery naphtha or LCO fractions also?

A 29. Standard ZSM-5 mainly cracks straight chain C6-C10 molecules, which are generally in the gasoline range, and will not crack "LCO". However, in cases of extreme undercutting of gasoline into LCO, i.e. the front end of the LCO contains C10- molecules, some conversion is possible.

Straight run, wild naphtha, slops or other naphtha range feeds can be routed to the FCC, in which case ZSM-5 will crack straight chain C6-C10 molecules in those feedstocks too.

JM would like to thank you for participating in this Webinar