



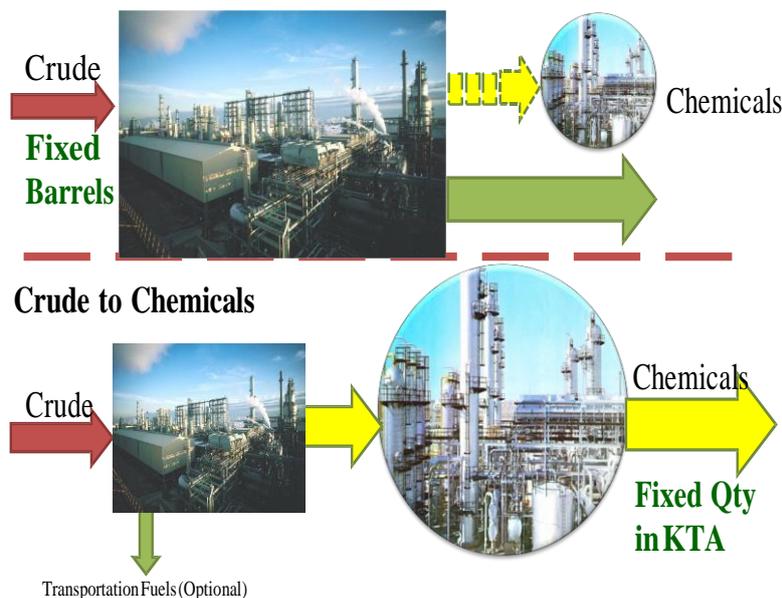
Crude Oil to Chemicals

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1.0 Introduction

The immediate future of refineries producing transportation fuels only is beset with uncertainties. Globally, refined products such as gasoline and diesel is growing in the range of 0.5 to 1.5%. Europe continues to be a major consumer of diesel despite the emission scandals that has seen a steady progression of major cities banning diesel cars in the near future. China is exporting diesel. India is also exporting diesel although this market will be a major consumer of diesel over the next decades as road infrastructure sees dramatic improvement and the GDP continues to rise at a pace of around 7%. Barring sudden local environmental restrictions such as those we see in Western Europe, diesel is intimately tied to the GDP growth of a country unlike gasoline that is very much linked to personal consumption. Gasoline consumption will experience downward pressure with more Electric Vehicles and especially hybrids entering the automobile sector but most global projections do not see the overall impact of EVs and hybrids exceeding about 5000 barrels/day by 2030 or roughly 5% of the overall petroleum products market; gasoline demand in 2030 is still expected to be around 30 million barrels/day. The last major transportation fuel is jet fuel and this fuel will see a flat to modestly upward growth, especially near major airports. Even as the demand for transportation fuels flattens, the impending IMO Sulfur Specification on Bunker Fuel Oil of 0.5 wt.% will put further pressure on those refineries that do not have advanced residue upgrading technologies or at the very least, a Delayed Coking unit. The price of high sulfur fuel oil will see a marked drop well below the crude price line as outlets for high sulfur fuel oil dry up. Installing scrubbers on ships is an unpopular and marginal solution to what needs to be with the large amount of high sulfur residue that will need upgrading from existing refineries. New refinery projects will all be designed with either the capability to produce ultra- low sulfur fuel oil or to eliminate bottoms altogether with sophisticated residue conversion units. Against this backdrop, the petrochemicals sector looks rosier. The global growth in petrochemicals is expected to be in 3-5% range. Volatility in crude oil prices can be greater than 100%, while those of major polymers are significantly lower at ~40%. There is thus the pressure on oil producers and major refiners to convert as much of the crude to chemicals as possible to increasing margins and to have a more predictable uplift. The easiest pathways to chemicals remain converting ethane from natural gas to ethylene or converting naphtha to ethylene and propylene. Why convert crude to chemicals? Crude to chemicals provides a strategic option of valorizing crude when the transportation fuels market is uncertain. Gas, plentiful in the United States is often scarce in regions where crude is abundant. The supply of cheap naphtha may tighten as refiners increasingly use this raw material for chemicals production, especially in Asia. Crude to chemicals provides a refiner with options to change the ratio of chemicals

to fuels depending on market needs. This paper leads the reader through the various commercially viable routes to converting crude to chemicals.



Converting crude to chemicals requires a complete change in mindset. In a conventional refinery with petrochemicals, the crude throughput is first fixed either in barrels/day or Million metric tons/annum and the desired transportation fuels are produced. Excess naphtha or other low value streams are routed to petrochemicals. In the Crude to Chemicals scenario, the type and quantity of chemicals to be

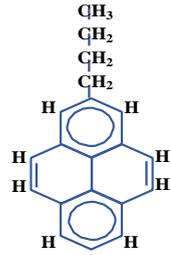
produced is first fixed. Next the amount of transportation fuels required, if any, is determined and then the required amount of crude to meet the demand of petrochemicals and optional transportation fuels – is calculated.

Challenges of Converting Crude to Chemicals

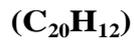
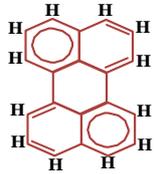
Bulk petrochemicals such as ethylene and propylene are made most readily from low molecular weight normal paraffins such as ethane, propane, butane, pentane, etc. through steam cracking. As the carbon number and boiling point of the petroleum cut increases, naphthenes and aromatics start appearing. Aromatics produce no olefins but rapidly coke up the pyrolysis heaters. Heavier aromatics and especially heavy polynuclear aromatics should never be fed to cracking heaters. As we move into the atmospheric and vacuum gas oil range, the heavier aromatics including multi-ring aromatics including condensed ring structures start appearing. Finally, in the residue boiling range, typically above 550°C+, polar multi-ring aromatics with alkyl chains (resins) and even higher molecular weight aromatic clusters called asphaltenes appear in large proportions.



or



or

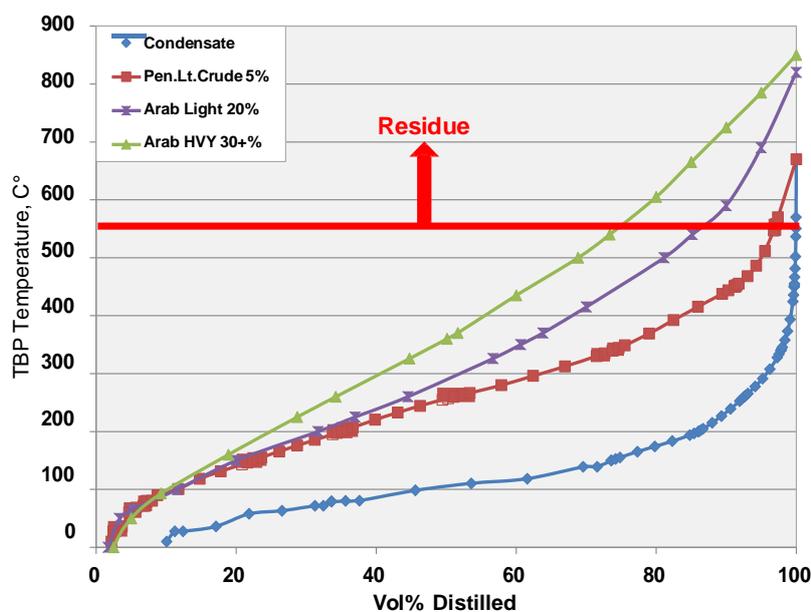
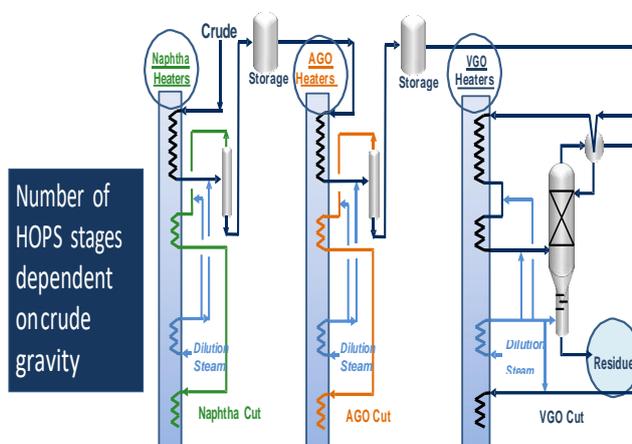


The figure on the left shows the complexity of converting a compound of Carbon Number 20. The normal paraffin will convert easily to very high yield of ethylene and boils around 320°C. The aromatic structures with the same number of carbon atoms could be boiling anywhere from 430°C to well over 550°C and be impossible to convert because of extremely short pyrolysis heater run lengths.

Heavy Oil Processing Scheme or HOPS

Lummus developed Heavy Oil Processing Scheme (HOPS) in the 1980's as a way to utilize whole crudes directly in steam crackers, bypassing conventional refinery units. In HOPS, the whole crude is preheated in the convection section of the steam cracker and flashed. The flashed vapor is mixed with steam and after controlled heating in the convection section is sent to the pyrolysis reaction section for conversion to olefins. Four units were designed and three are still in operation. There are several factors that influence both the number of HOPS stages and the routing of flashed lighter fractions to different heaters. Crude is a mixture of very wide boiling components. For example, if VGO and propane are cracked in the same heater, and the severity is maximized for VGO cracking the propane will be under cracked (below maximum propylene). The HOPS in combination with the steam cracker convection section permits the crude to be separated into fractions that can be sent to the pyrolysis reaction section together for maximizing the yield of olefins.

For example, if we wanted to maximize the yield from a combination of naphtha, atmospheric gas oil and VGO, we would recommend a 3-Stage HOPS. As was mentioned earlier, steam cracking of residue components would lead to very rapid fouling of heater tubes and very low yield of olefins. Thus, direct crude cracking without pretreatment is suited only for crudes with very small fraction boiling in the residue range (typically above 540°C) or condensates.



The figure on the left illustrates the challenge of whole crude cracking. As the crudes become heavier, more of the residue has to be rejected and without an adjoining refinery to upgrade this residue, the stream has no outlet other than as high sulfur fuel oil. Even this outlet will disappear post 2020 with the new IMO regulations on sulfur.

The Benefits of Hydrogen Addition

Even if we were able to process the whole raw crude in cracking heaters, we still have to examine whether the olefin yield is competitive in comparison to yields from more traditional feedstocks such as naphtha.

Table 1, shows the typical yields from a steam cracker for various straight-run feeds compared to unconverted oil from a partial conversion hydrocracker.

	Full Range Naphtha	AGO	VGO	Isocracked VGO
CH ₄	15.40	10.90	9.20	12.60
C ₂ H ₄	29.00	24.50	13.50	30.00
C ₃ H ₆	13.50	13.30	12.00	13.30
C ₄ 's	8.70	8.85	7.85	8.60
C ₅ -204°C	21.20	19.05	16.60	19.00
F.O.	5.60	18.16	37.45	10.10

Table-1

Not only does the hydrocracked VGO produce far more ethylene than straight-run VGO, it also produces far less of pyrolysis Fuel Oil (F.O.). The Pyrolysis Fuel Oil is a highly aromatic, low hydrogen content stream that typically has no outlet other than as internal fuel oil. Hydrocracked VGO produces almost as much olefins as straight-run full-range naphtha.

Table-2 shows the typical yield of olefin products from a hydrocracker (using CLG ISOCRACKING technology) operating at ~65% conversion. The light naphtha and unconverted oil are excellent feedstocks for Steam Crackers and the heavy naphtha a good feed for a Catalytic Reforming unit. The kerosene and diesel streams are best suited for transportation fuels.

	Light Naphtha	Heavy Naphtha	Kerosene	Diesel	Isocracked VGO
CH ₄	16.00	12.80	11.00	12.20	12.60
C ₂ H ₄	29.00	23.80	23.00	27.00	30.00
C ₃ H ₆	14.00	12.85	13.50	13.40	13.30
C ₄ 's	9.55	10.30	8.80	8.85	8.60
C ₅ -204°C	19.50	26.20	21.15	18.75	19.00
F.O.	4.83	7.85	17.53	14.07	10.10

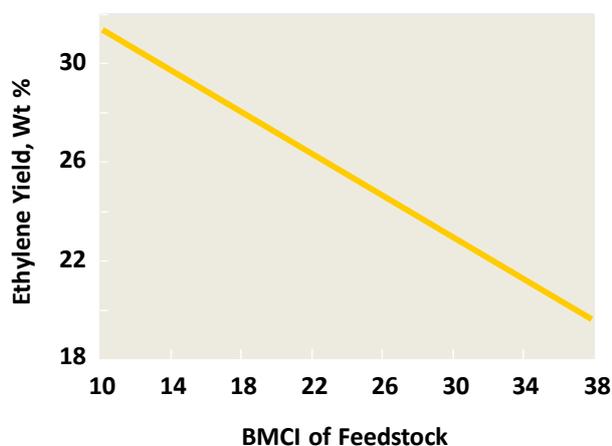
Table-2

Clearly, the addition of hydrogen is beneficial to conversion of oils to chemicals. Paraffins that have the highest hydrogen content, produce the highest olefin yield from crackers. Light naphtha and unconverted oil at relatively high conversions and high-pressure operation, are rich in paraffins and produce the highest ethylene yields. One measure of the degree of hydrogenation of unconverted oil is the Bureau of Mines Correlation Index or BMCI. Lower the BMCI, the higher the yield of ethylene.

$$\text{BMCI} = 473.7 (\text{Sp. Gr.}) - 456.8 + (87552/\text{MABP})$$

Sp. Gr. = Specific Gravity at 15/15°C
MABP = Molal Average Boiling Point, °R

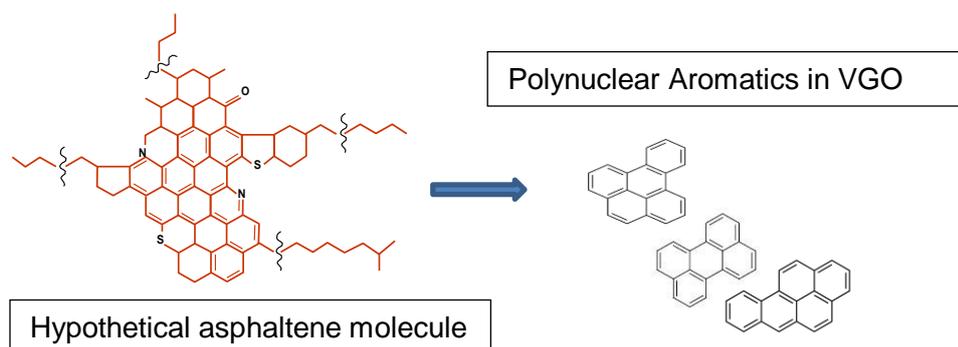
Lummus has designed Steam Crackers with a wide range of gas oils with BMCI ranging from 2 to 42. A high-pressure hydrocracking unit with relatively high conversion will produce BMCI in the 8-10 range for Straight-run VGO feeds. The advantage of producing unconverted oil with low BMCI is that this oil will also be an excellent feedstock for Lube Oil Base Stock production. Mild hydrocrackers operating at lower pressure and relatively low conversion, <50%, will produce unconverted oil with low sulfur, low nitrogen, and good hydrogenation suitable for a FCC unit but with relatively high BMCI (20-45) resulting in low ethylene yields and unsuitable for steam crackers.



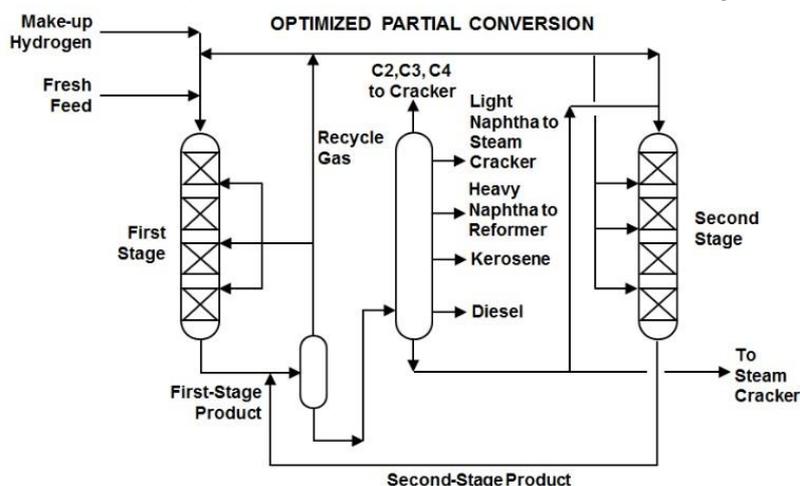
The other factor that is extremely important is the nature of polynuclear aromatics still present in the unconverted oil. Advanced analytical techniques utilized by CLG (HPLC-MS and HPLC-UV-ELSD) identify signature heavy polynuclear aromatics (HPNA) at very low concentrations.

Just a few parts per million of HPNA such as coronenes can dramatically reduce the run length of steam cracker heater tubes and/or foul the Transfer Line Exchanger (TLE).

Straight-run VGO with high end points (>550°C) have 5-ring aromatic compounds. This can grow to 7,9,11+ rings in hydrocracking unless we have the correct catalyst system and hydrocracking operating environment. With any crude to chemicals campaign dealing with light, medium or heavy crudes, residue hydrocracking becomes an essential component of feed preparation for downstream petrochemicals. Residue hydrocracking requires conversion of asphaltenes and irrespective of the technology employed the Vacuum Gas Oil derived from Vacuum Residue at quasi-total conversion will be rich in 4 and 5 ring polynuclear aromatics. The VGO needs to be hydrocracked so that the resulting naphtha can be converted to aromatics and/or olefins in catalytic reforming and/or steam cracking.



Hydrocracking to very high conversion of residue hydrocracking-derived VGO requires special expertise in both catalyst and process technology. CLG is the only process licensor with commercially operating integrated hydrotreating and hydrocracking units. CLG recommends and uses its Optimized Partial Conversion (OPC) for High Conversion of VGO from Residue Hydrocracking.

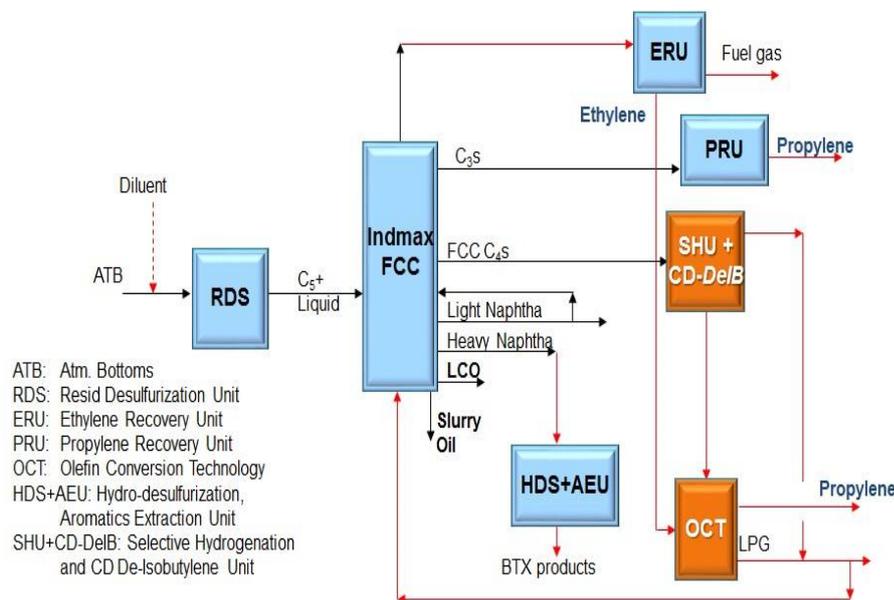


The hydrocracker is thus one of the most important components in the overall Crude to Chemicals strategy. The technology is extremely versatile and can maximize heavy naphtha rich in naphthenes and aromatics for maximizing feed to catalytic reforming, produce high quality

transportation fuels or lube oil base stocks, or in maximum severity mode, convert all the VGO and Diesel range material to naphtha suitable for a steam cracker.

The RDS-RFCC Route

Atmospheric or Vacuum Residue can be desulfurized and fed to a RFCC unit designed to maximize propylene. This configuration has the advantage of minimizing hydrogen consumption and has the potential of maximizing propylene.



If there is a demand for gasoline and some diesel and a good market for propylene, the RDS-RFCC is an excellent configuration. The RDS being a fixed bed system will usually have multiple trains so that the unit can continue running when one train is down for catalyst changeout, usually every 11-13 months.

The turnaround schedule and capacity factors have to be carefully planned so that feed to the downstream chemicals production is never compromised.

The main drawbacks of this scheme are the following:

- All of the crude cannot be converted to chemicals; there will always be some transportation fuels that have to be produced. Any Light Cycle Oil from the RFCC, usually blended with straight-run diesel and severely hydrotreated to produce Euro VI diesel.
- There is no outlet available for the Heavy Cycle Oil from the RFCC or the Pyrolysis Fuel Oil from the Steam Cracker other than as low-grade fuel oil with very limited outlets.
- There will be a substantial amount of gasoline production.

Commercially Viable Configurations Based on Proven Technology

Figures 1 and 2 depict configurations with the most commercially proven Residue Hydrocracking technology called LC-FINING from CLG. Conversion typically ranges from 60 to 85%. The unconverted oil from the LC-FINING unit can be sent to a Delayed Coking Unit for incremental conversion to Heavy Coker Gas Oil and lighter material that can be further upgraded to Steam Cracker and/or Catalytic Reformer feed utilizing the versatile ISOCRACKING technology. The LC-FINING unit placed upstream of a Delayed Coking Unit enables the complex to produce low sulfur pet coke that often meets the green coke requirements of anode grade coke.

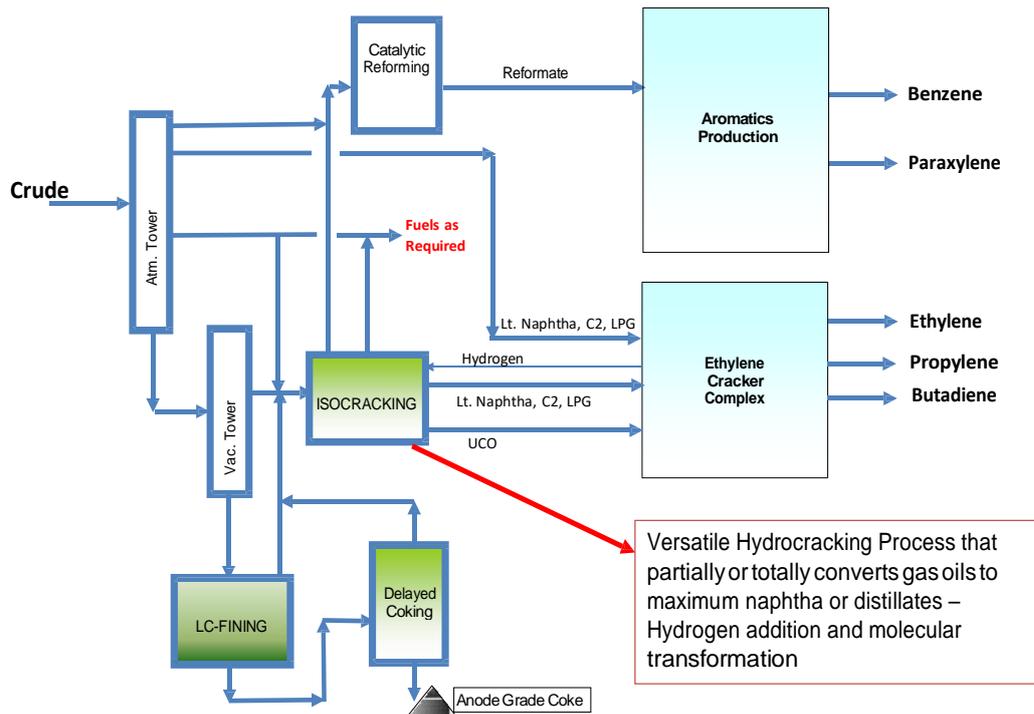


Figure-1

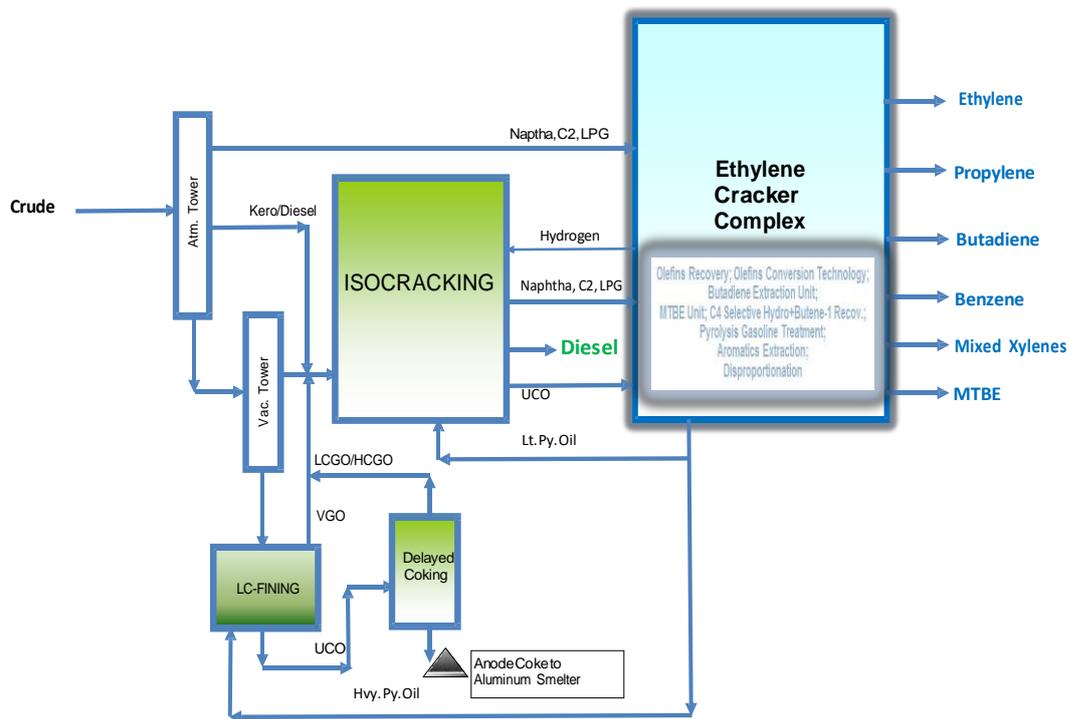
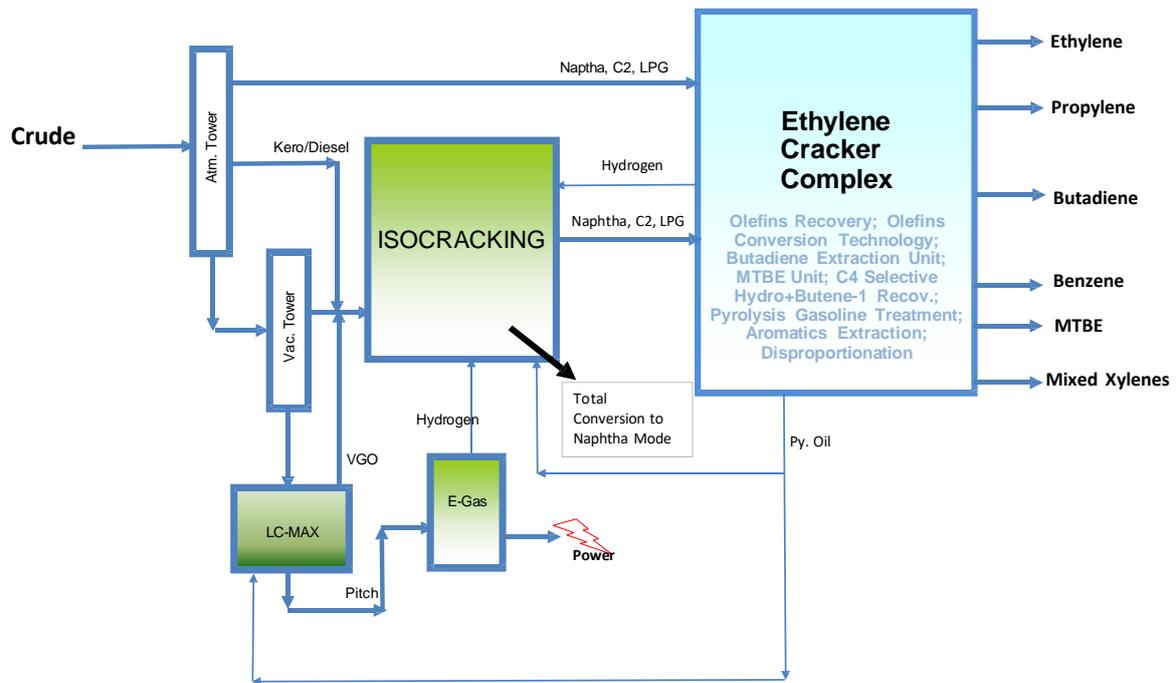


Figure-2

Figure-3 shows a configuration with LC-MAX where VR conversion can be extended to nearly 93%. The pitch from LC-MAX can be sent to gasifier for production of hydrogen and power. LC-MAX uses two LC-FINING reaction stages with an intermediate solvent deasphalting step to reject the most hydrogen-deficient asphaltene molecules. The patented process was first licensed in 2013 and since then, three new licenses have been awarded to CLG.

Figure-3



For complete conversion of residue, the LC-SLURRY process that uses the same liquid circulation platform as LC-FINING, but instead of extrudates used in LC-FINING and LC-MAX, uses a proprietary slurry catalyst called ISOSLURRY. The first LC-SLURRY unit was licensed in 2016 to Beowulf/Preem in Sweden. Figure-4 represents a crude to chemicals configuration utilizing LC-SLURRY.

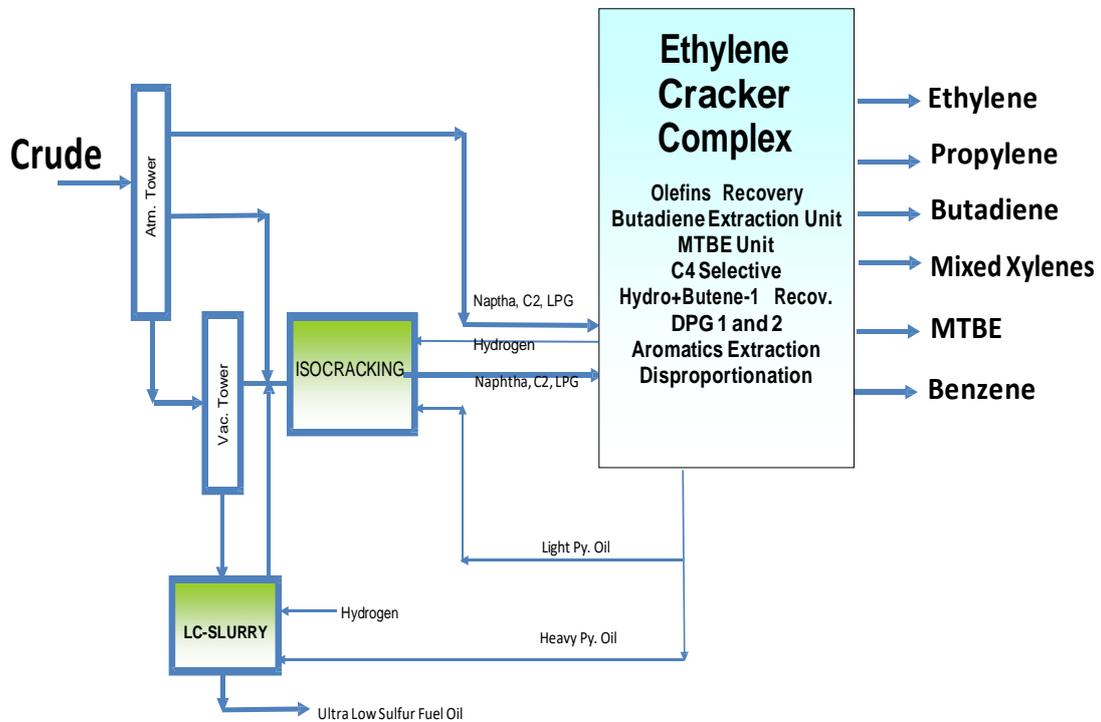


Figure-4

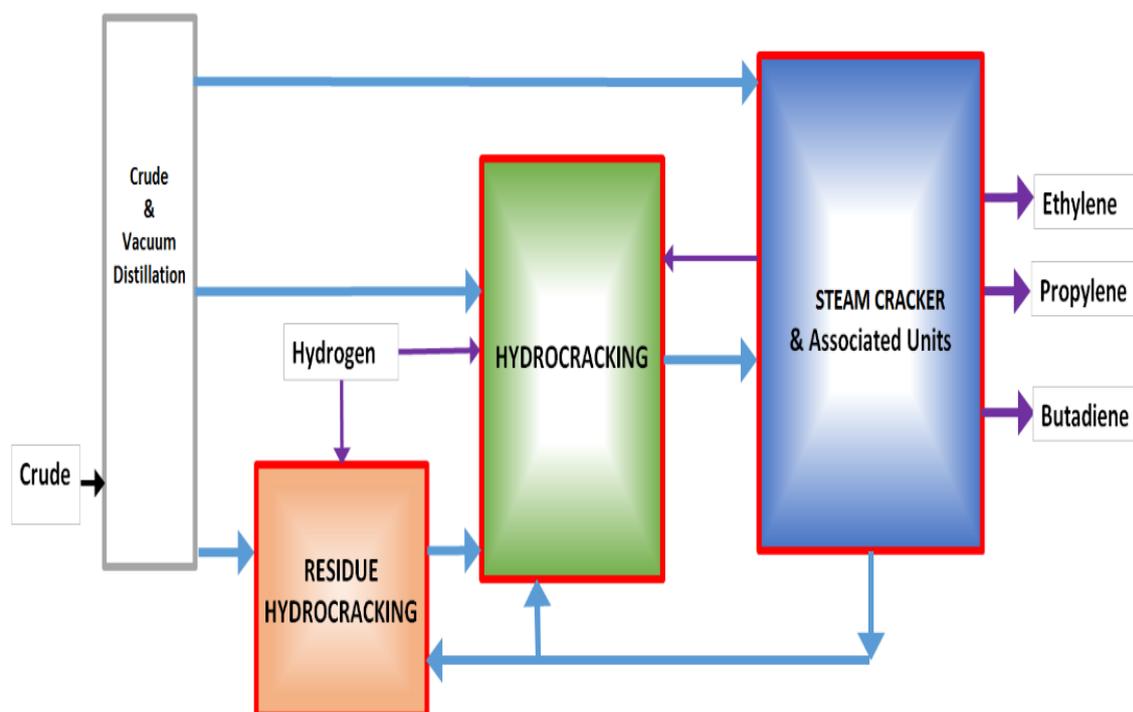
In all the LC- configurations, the Pyrolysis Oil from the Steam Cracker can be processed in to produce incremental Steam Cracker feed or transportation fuels. The configuration thus significantly reduces the production of orphan streams.

Table-3 shows the comparison of various residue hydrocracking options in the production of chemicals and transportation fuels:

	Minimum Investment; No Resid Upgrader; No Fuels; Sell HSFO	LC-FINING; No Fuels; Sell LSFO	LC-FINING With Fuels; Sell LSFO	LC-FINING With Fuels; Sell LSFO - Two Train Cracker	LC-FINING + Delayed Coking; No Fuels; Produce Anode Coke	LC-Slurry With Fuels; Produce ULSFO
Crude (Arab Light), BPD	195,000	162,000	227,000	400,000	137,689	246,515
Ethylene, KTA	2,000	2,000	2,000	4,000	2,000	2,000
Propylene, KTA	1,480	1,493	1,469	2,805	1,481	1,489
Butadiene, KTA	357	358	347	774	373	326
Euro VI Diesel, BPD	0	0	74,500	94,265	0	106,000
Fuel Oil, BPD	54,000	25,000	20,000	36,935	0	8,500
Anode Coke, KTA	0	0	0	0	194	0
H2 Required, MMSCFD	167	251	379	665	282	417
% Required H2 from Cracker	39	26	18	22	24	16
Natural Gas Required, KTA	596	777	1,011	1,872	794	992
Chemical Yield on Crude, %	58	70	49	57	83	45
Total Project Cost, MM\$	6,954	7,995	8,910	14,173	8,492	9,285
%IRR	14.6	22.4	24.4	33.0	21.4	25.0
Notes						
	1. 3% HSFO	1% S LSFO	1% S LSFO	1% S LSFO	Anode Coke	0.1% S ULSFO
	2. All cases includes Hydrocracker + Olefins Conversion Technology					
	3. All cases produces MTBE, Butene-1, Benzene, Xylenes					
	4. 3% HSFO priced at \$21/Bbl less than crude					
	5. %IRR based on 70 / 30 debt / equity ratio					

Table-3

The table shows that a world class chemicals production facility can be supported with just 137,000 barrels/day of crude oil. The core technologies for a successful crude to chemicals project remain Residue Hydrocracking, Hydrocracking and a Steam Cracker.



Summary

Crude to Chemicals requires a different mindset. We must first focus on the quantity and type of chemicals that makes economic sense for a particular region and then work back to the amount of crude required. Petrochemicals units such as Steam Crackers have very precise feedstock quality requirements especially in the gas oil range. The complex will require very high on-stream factor in classical refining technologies to match the high on-stream factor of petrochemicals units. A Crude to Chemicals complex has to be designed with both crude and product flexibility in mind. In times of high diesel demand for example, it would not be economically justified to destroy diesel in favor of making naphtha for petrochemicals. In terms of crude slate, a balance between light and heavy crude slate will offer the best balance between capital and operating costs. In every scenario, high residue conversion is necessary as is the need to not have any orphan low value stream such as slurry oil or pyrolysis oil leaving the complex. Direct Crude cracking to chemicals using HOPS technology is viable for condensates and very light crudes. RDS-RFCC remains attractive when both the gasoline and propylene markets are robust. Residue Hydrocracking offers the maximum conversion and crude flexibility. At the heart of the Petrochemicals Feed Preparation is hydrocracking. This versatile technology can vary the product slate from maximum petrochemicals feed to a balance between transportation fuels and petrochemicals feed and offers the possibility of producing high value lube oil base stocks. Finally, a world class mixed feed cracker with an adequately sized refinery provides the highest return on investment and maximum product flexibility in a Crude to Chemicals project.