

Technical & Commercial Progress in the Global Catalytic Process Industries



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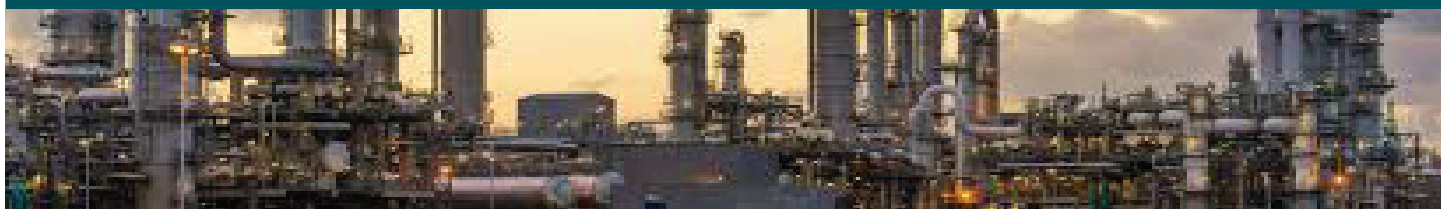
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## Oil-to-Chemicals: New Approaches from Resid and VGOs



Industry Perspectives: Simplifying Nitration Chemistry with a Bench-stable and Easily Accessible Reagent





## Oil-to-Chemicals: New Approaches from Resid and VGOs

By John J. Murphy and Clyde F. Payn

Crude Oil-to-Chemicals (COTC) continues to be a powerful industry driver, and a strong trend of high interest to all integrated refineries and chemicals producers in Asia/Pacific, China, the Middle East and Eastern Europe! This is reinforced by many factors, most notably the forecasts which predict a slowing of transportation fuels growth approaching 2040 (with hybrids and EVs), while the growth in chemicals is expected to increase as the population and middleclass wealth continues to rise, leading to increasing demand for packaging, consumer goods and automobiles.

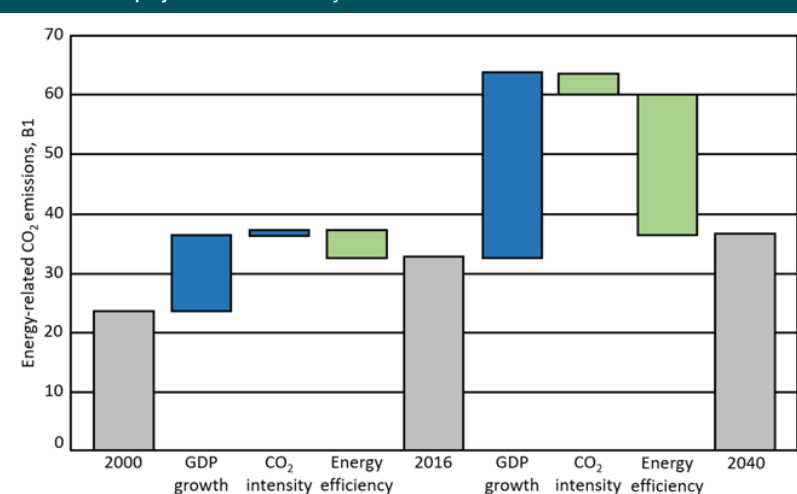
Are you aware that more than 12 corporations have committed over \$315 billion to date to reconfigure their assets to produce more petrochemicals than transportation fuels, as revamps as well as to build new grassroots refineries during the next 5-6 years! Based on announcements to date, we anticipate in the next five years that another \$300+ BIL, or more, will also be announced as refiners and chemical companies all reassess their positions, knowing that the longer-term outlook for transportation fuels from crude oil is expected to plateau and then decline. All players are taking this trend seriously and therefore you should also!

There is considerable flexibility being offered by petrochemical licensors, in particular petrochemical Resid and VGO FCC upgrading units today. These are global changes including deep catalytic cracking (DCC) from Sinopec, as well as Western leaders such as TOTAL's R2R modifications, and Axens' high-severity FCC (HSFCC) with Saudi Aramco. Technologies do not stand still. Advances in catalytic visbreaking may also be important in the future, when looking into advanced lower cost alternatives and we have examined these R&D pipelines.

Already a large number of companies are closely examining their own responses and investments, bearing in mind each of these investment objectives will be site specific, influenced by feedstock choices, product slates/markets, energy/utility balances, capital/operating efficiencies, and health, safety and environmental (HSE) performance. It is clear from public domain information (e.g., the ongoing announcements by ADNOC, MOL and others) to see the progress in differentiation that is already underway.

Of the two main interests of producers, are: 1) to decrease the capital intensity through scale, simplicity and location; and 2) expand/maximize flexibility towards use of current (heavier) feedstocks in considering the "oil-to-chemicals" approach. The idea that better utilizing assets from within an integrated refinery site means that most likely you are already dealing at 10x, plus, the size of a world-scale petrochemical plant. Although scale counts, it is also only one of the many factors. New advanced configurations will now start to incorporate the planning of improved efficiency gains and reduced CO<sub>2</sub> emissions, as well. ExxonMobil, in its 2018 Outlook for Energy, forecast that by 2040, while energy efficiency gains are expected to nearly double, carbon emissions are only projected to increase by a modest 10%. BP statistics, along with Chevron forecasts, IEA and EIA, also show similar trends (see **Figure 1**).

**Figure 1.** Energy efficiency gains are expected to nearly double by 2040, while carbon emissions are projected to increase by a modest 10%.



Source: ExxonMobil 2018 Outlook for Energy.

Regarding competitive crude-oil-to-chemicals (COTC) developments, in addition to Saudi Aramco/SABIC announcements, we are already seeing ongoing investments from others. In a more recent example (Hydrocarbon Processing, 2018), private chemical producers Hengli and Rongsheng in China are back-integrating their chemical plants to add over 9 MIL mt/yr of paraxylene (PX) capacity by 2021. This is expected to reduce PX imports by 4 MIL mt/yr, with plans to yield up to 45 wt% of chemicals processing heavy crudes, which will tighten medium to heavy crude markets while also adding a 40% surplus to distillates and gasoline markets.

One of the most difficult components has been to understand that all licensors need to prioritize their own businesses. Therefore, they will prefer greenfield investments to revamps—even if these can be accomplished at lower ISBL and OSBL costs. This is not a criticism but rather a statement in fact based on desired business focus. Moreover, one of the understandings is to appreciate how existing and new configurations can be tailored towards either aromatics or olefins—but this may not be the best measure if indeed your goal is towards more olefins. In this regard, assuming you have an existing steam cracker, your revamp approach maybe quite different.

### **Advances to Heavy Oil Processes**

In focusing on the processes by which the higher molecular weight constituents of petroleum (the heavy ends) can be converted to products that are suitable for use of feedstocks to the petrochemical section of the refinery, the assessments are broken into groups to include carbon rejection and hydrogen addition approaches along with process combinations and new configurations.

1. Carbon Rejection
2. Hydrogen Addition
3. Combining Processes and Treatment of Intermediates
4. Configuration Issues and Advances
5. New Processes Likely to be Deployed During the Next Five Years

Highlights addressing potential deployment of technology advances, including combinations and configurations include:

- For decades, propane has been the mainstay used extensively in deasphalting heavy feedstocks, especially in the preparation of high-quality lubricating oils and feedstocks for catalytic cracking units. Future units, which may well be derived from the ROSE™ process, will use solvent systems that will allow operation at elevated temperatures relative to conventional propane deasphalting temperatures, thereby permitting easy heat exchange. This will require changes to the solvent composition and the inclusion of solvents not usually considered to be deasphalting solvents. Other areas of future process modification will be in the extractor tower internals, studies with higher molecular weight solvent, accurate estimation of physical properties of mix stream, studies in combination with other processes and firming up design tools for supercritical solvent recovery configuration.
- For the heavy feedstocks, which will increase in amounts in terms hydrocracking feedstocks, reactor designs will continue to focus on online catalyst addition and withdrawal. Fixed bed designs have suffered from (i) mechanical inadequacy when used for the heavier feedstocks and (ii) short catalyst lives – six months or less – even though large catalyst volumes are used (LHSV typically of 0.5 - 1.5). Refiners will attempt to overcome these short-comings by innovative designs, allowing better feedstock flow and catalyst utilization or online catalyst removal. For example, the OCR process, in which a lead, moving bed reactor is used to demetallize the heavy feedstock ahead of the fixed bed hydrocracking reactors has seen some success. But whether this will be adequate for continuous hydrocracking heavy feedstock remains a question.
- Catalyst development will be key in the modification of processes and the development of new ones to make environmentally acceptable distillable liquids. Although crude oil conversion is expected to remain the principal future source of petrochemicals, natural gas reserves are emerging, and will continue to emerge, as a major hydrocarbon resource. This trend has already started to result in a shift toward use of natural gas (methane) as a significant feedstock for chemicals. As a result, deployment of technology for direct and indirect conversion of methane will probably displace much of the current production of liquefied natural gas.
- The detrimental effects of coke are a reduction of support porosity, leading to diffusional limitations, and finally blocked access to active sites. Nevertheless, moving bed or ebullated bed processes alone or in combination with fixed bed reactor technology and/or also coupled with thermal processes employing suitable catalyst with metal retention capacity represent the most efficient way of handling petroleum bottoms and other heavy hydrocarbons for upgrading. The features of the resulting process configuration will be high liquid yields, high removal of contaminants, and reliable operation.

### **Holistic Economics and Approaches to Complexes**

From a comprehensive or holistic perspective, the following approaches have been assessed as commercially viable or considered to become commercially viable in specific situations.

1. New Pipeline Technology Considerations
2. Advances in New Configurations
3. New Catalyst Approaches
4. Economics of Different Catalysts and Process Improvements

## Competitive and Strategic Implications

In reviewing some of the key findings from the report, as well as the limits that current State-of-Art (SoA) based on the basket of crudes defined in the report, here are some key considerations:

- No study can take into account all possible site-specific issues and questions, as they may relate to existing configurations for revamp vs greenfield choices because they are highly dependent on each refinery's crude slates, availability/pricing and the local/regional products desired. Given this situation, this study takes a 10,000ft view, looking into the hypothesis of a 50/50 fuels/petchem refinery, and then discusses future technology options/changes in the pipeline in the direction for 40/60 fuels/petchem. Today's Resid FCCs can process feeds with up to 8 Concarbon, though 6-7 is more comfortable. Today's RFCCs are designed for catalyst metals levels of 10,000 ppmw. However, it is cheaper to take the metals out on an HDM pretreater catalyst which holds up to 50% of their weight in metals. A standard design is to include an extra riser for making olefins. A 100,000B/D RFCC can make over 500,000 mt/yr of propylene, assuming a 10wt% yield. Additional technologies can increase this to 30-40wt%. For instance, VGO processing with an HDM/HDS unit can give around 29% propylene. The FCC gasoline, which is about 50wt% BTX, can also be partially processed in the aromatics plant. Fine tuning in the RFCC for C3= is a lot less costly than PDH.

Figure 2. Refinery-Petrochemical Integration.



- When processing heavier feedstocks, the consensus is to have hydrogen-in revamps or greenfield designs.
- Increasing the severity of RDS/RFCC to produce more C3= decreases both gasoline and diesel yield. Forwarding heavy naphtha is required for reformat feed to aromatics. Improving liquid yields can be done with different degrees by upping VGO+DAO, while reducing coke to almost zero.
- Smaller (100K bpd) refineries won't be as likely to have the capital to integrate like the >250K and larger sites.
- All licensors, by their remits, will try and sell you on complex greenfield site configurations based on their competitive advantages (e.g., UOP in aromatic complexes). Others have different revamp expertise e.g. Shell. When we use examples throughout our analyses, they are to highlight real world examples. We are doing our best to be independent, and we are not recommending or defending any technologies by any supplier. This will be up for you to decide, based on deeper CDA based discussions.

Critical to an assessment of the potential for oil-to-chemicals is the number and types of committed investments to date (2019). This study documents those announced investments declared during the last five (5) years as oil-to-chemicals projects, along with company, location, size of project, and \$ investment. Where available and announced we have also included the wt.% fuel vs chemical targets (see **Table 1**). These all have been more closely researched, with Sources and Notes provided. What it does highlight is there are at least \$315 BIL in already committed investment, of which \$100 BIL are in revamps. \$120 BIL in China, and \$82.7 BIL in Asia/Pacific, and \$108 BIL in the Middle East.

There are project examples where these considerations have already been reviewed. For example, MOL Petrochemicals, Tiszaujvoros, Hungary, has decided to upgrade its 100,000 MTPa to produce more polymer grade propylene from steam cracking and refinery feedstocks (MOL, 5/24/18 PR). In doing so it has chosen two steps utilizing Lummus OCT and a CDHydro Deisobutenizer, which will generate an isobutene-rich stream, whereas the OCT will generate increased propylene production. These modifications are reportedly available for less than <\$50MIL. Also, the MOL revamp is interesting as intends to incorporate Innovacat swing fixed bed technology in the refinery.

Another example we highlight, which we think stands out with some interesting conclusions, is the revamp for the Polish refiner Grupa LOTOS, when in 2011 it installed and made operational a new generation of DAO hydrocracking technology as part of a major resid upgrading project called the 10+ Programme. In this case, it raised refining capacity by 75%, focused on higher margin diesel fuels to increase market share and enhanced margins by \$5 per barrel.

In this case, the two units added by Shell Global Solutions were a 45,000 bpd DAO hydrocracker using 50/50 VGO/DAO straight off these units, with the added DAO unit. What is interesting using Urals feedstock is that the hydrocrackers, inclusive of both HDM, HDS and HDN, were able to increase conversion to 85% from 60% with a recycle mode.

Based on the information from these examples and assuming the VDU and ADU are already in place investments, then, an SDA unit (KBR, Rose, or Axens Hyvahl or SELEX-Asp) depending on the product slate chosen, is a considered first step at a lower approximate cost of \$250-280 MIL. The following issue depends on how much existing HDM, HDS and HC capacity that exist.

## Recommendations and Conclusions

In summary, there has been a long history in the incremental developments (decades in fact) leading to what can be described as “Oil-to-Chemicals (OTC).” For a long period of time, building larger and larger world scale and more complex refineries and steam cracking (SC) plants was the economic solution best suited to the fundamentals of medium to heavy crude oil conversion, and in some countries, this will still be the case. However today, we have entered a different era, where the socioeconomic, as well as supply/demand trends are shifting, and the traditional business models of segregated refining vs chemicals production no longer hold true

The ongoing drive for improved profitability profiles, derived by producing petrochemicals as opposed to fuels, has justified the increased pace of the O-t-C movement. Not only are demands for olefins and aromatics growing more quickly than gasoline and diesel, the profit margins for these petrochemicals are also higher, and even more so when made directly via O-t-C conversion routes.

Although moderate to date, the commitments to these plant configurations will require retrofits as well as new CAPEX using skilled laborers and EPCs. As the former are limited and the latter is notoriously cyclical (as is the energy/fuels industry), it is important to assess how large and when these events will impact the availability of (and price for) skilled labor. To what degree will envisioned projects be delayed or their price increase, as a result?

The two O-t-C approaches – carbon out and hydrogen in – have implications across related technologies. Coking will remain a “go to” for carbon-out with any advances having outsized impacts (due to the breath of implementation, e.g., delayed coking); hydrogen supplies will need to increase or become more flexible (without additional energy/CO<sub>2</sub> impacts) in order to address the range of upgrading requirements.

Table 1. Announced Oil-to-Chemicals Investments 2019.

Company	Location	Cost (\$BIL)	Type	Projected Start up
China				
Zhejiang Petroleum and Chemical <sup>1</sup>	Zhoushan, China	\$26	Greenfield	2019 (Phase 1)
Hengli Petrochemical <sup>1</sup>	Changxin Island, China	\$11	Greenfield	2019
Shenghong Petrochemical <sup>1, 2</sup>	Lianyungang, China	\$11.84	Greenfield	2019
Ningbo Zhongjin Petrochemical (subs Rongsheng Petrochemical) <sup>3, 4</sup>	Ningbo, China	\$5 (est)	Revamp	2018
Saudi Aramco/NORINCO/Panjin Sincen (Huajin Aramco Petrochemical) <sup>5</sup>	Liaoning Province, China	\$10+	Greenfield	2024
SABIC/Fuhaichuang Petrochemical <sup>5</sup>	Zhangzhou, China	NA	Greenfield	NA
SINOPEC/SABIC (Tianjin Petrochemical) <sup>6</sup>	Tianjin, China	\$45 combined (est)	Revamp	Operating, pre-2017
PetroChina <sup>6</sup>	Dakan, China		Revamp	Operating, pre-2017
PetroChina <sup>6</sup>	Yunnan, China		Revamp	Operating, pre-2017
CNOOC <sup>6</sup>	Huizhou, China	\$2.8	Revamp	Operating, pre-2017
SINOPEC <sup>6, 7</sup>	Lianyungang, China		Greenfield	NA
SINOPEC <sup>6, 8</sup>	Caoheidian, China		Greenfield	NA
SINOPEC <sup>6, 9</sup>	Gulei, China	\$4.26	Greenfield	2020
Total China:		\$120.1		
Other Asia				
Hengyi Group <sup>3</sup>	Pulau Muara Besar, Brunei	\$20	Greenfield	2020
Saudi Aramco/ADNOC/India Consortium <sup>5</sup>	Raigad, India	\$44	Greenfield	2025
Petronas/Saudi Aramco (RAPID) <sup>8</sup>	Pengerang, Malaysia	\$2.7	Greenfield	2019
ExxonMobil (Singapore Chemical Plant) <sup>11, 12</sup>	Jurong Island, Singapore	<\$1	Revamp	2023
Pertamina/Rosneft <sup>6, 13, 14, 15</sup>	Tuban, East Java, Indonesia	\$15	Greenfield	2025
Total Other Asia:		\$82.7		
Middle East				
ADNOC <sup>5</sup>	Al Ruwais, UAE	\$45	Revamp	2025
Saudi Aramco/SABIC <sup>5</sup>	Yanbu, Saudi Arabia	\$30	Greenfield	2025
Saudi Aramco/Total <sup>5</sup>	Jubail, Saudi Arabia	\$5	Greenfield	2024
KNPC/KIPIC (Al-Zour Refinery) <sup>16</sup>	Al Ahmadi, Kuwait	\$13	Greenfield	2019
Oman Oil Company/Kuwait Petroleum International (Duqm Refinery) <sup>17</sup>	Oman	\$15	Greenfield	NA
Total Middle East:		\$108		
Europe				
MOL Group <sup>14</sup>	Hungary, Croatia	\$4.5	Revamp	2030
Total Europe:		\$4.5		
Total Greenfield: \$215		Total Revamps: \$100		Total Global: \$315

Source: TCGR, 2019.



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- The Catalyst Group Resources (TCGR). (2019). "Oil-to-Chemicals II: New Approaches from Resid and VGOs." [http://www.catalystgrp.com/multiclient\\_studies/oil-chemicals-ii-new-approaches-resid-vgos/](http://www.catalystgrp.com/multiclient_studies/oil-chemicals-ii-new-approaches-resid-vgos/)

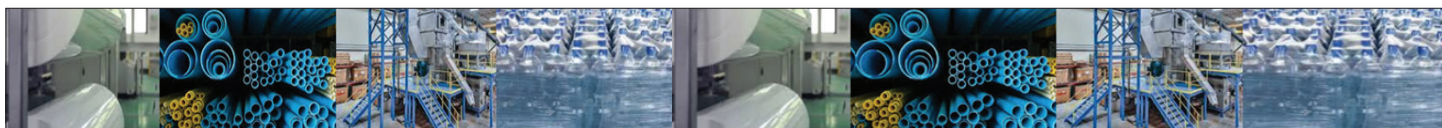
## About the Authors

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The above is excerpted from TCGR's multi-client study, "Oil-to-Chemicals II: New Approaches from Resid and VGOs," which was completed in June 2018. TCGR extends its original study in this area entitled, "Oil-to-Chemicals: Technological Approaches and Advanced Process Configurations" (completed in December 2017), to assess technologies, configurations and capex/opex metrics for olefins/aromatics production via resids, VGOs and heavier feeds.

TCGR is offering a discount of \$1,000 off "Oil-to-Chemicals II: New Approaches from Resid and VGOs" to subscribers of that study. Subscribers are requested to contact John J. Murphy at +1.215.628.4447, or [John.J.Murphy@catalystgrp.com](mailto:John.J.Murphy@catalystgrp.com) if further details are required or to determine if your organization is entitled. When completing the order form, please make sure to indicate your company's subscription to the earlier report.

Additional details can be obtained at [http://www.catalystgrp.com/multiclient\\_studies/oil-chemicals-ii-new-approaches-resid-vgos/](http://www.catalystgrp.com/multiclient_studies/oil-chemicals-ii-new-approaches-resid-vgos/)



## JUST ANNOUNCED!

### *Voice of the Customer Driving Innovation and Growth in Polyolefins Catalyst and Process Technologies!*

### **"Progress in Technology for Polyolefins Production III"**

As The Catalyst Group Resources (TCGR) has demonstrated via its multi- and select-client studies in the past, there is ongoing value-added in the R&D endeavor, whether it is (1) improved productivity from existing assets; (2) improving processes and obtaining value added from licensing or joint venturing cutting edge polyolefin catalyst or process advances; or (3) developing superior resins which can be sold for higher pricing. Indeed, the polyolefin industry has a rich history of innovation and the expectations for future advances are unquestioned.

Based on TCGR's groundbreaking study in 2011 entitled "Progress in Technology for Polyolefin Production: Quantifying the Value-Added of Advanced Catalysts, Co-Catalysts/activators and Stereo regulators" and two, more focused, updates in 2017 and 2018 (notably "Polyolefin Catalysts and Processes: Technological and Commercial Impacts on PE and PP" and "Polyolefins Catalysts and Processes: Competitive Implications of Industry Consolidation"), it is now time for a more in-depth and comprehensive industry reassessment.

In this proposed 2020 update, TCGR will revisit both the new product markets, as well as the R&D pipelines, documenting and analyzing opportunities of benefit to polyolefins (PO)

producers in their business planning and decision making. New/key to this updated study will be a comprehensive "Voice of Customer" survey on resin converters and the changing resin requirements to meet the future needs from within industry.

This study will document, through patent and literature surveys, detailed assessments of emerging technologies, product and process advances, and "voice of customer" surveys/interviews, the following:

- New and improved PO resins to serve the faster growing differentiated or "specialty" market applications, including large volume price-sensitive markets, as well as sophisticated niche applications
- Gains in production volumes from fixed

assets which can be achieved through recent improvements in processes and in catalysts, co-catalysts/activators and/or electron donor (ED) technologies

- Value-added returns on R&D, which can result from developing, licensing or joint venturing cutting-edge polyolefin process, catalyst, co-catalyst/activator and product advances
- New/key: A Voice-of-Customer survey with converters to understand the missing new product needs from within the marketplace

This proposed multi-client study is scheduled for completion in June/July 2020.

Additional information, including the complete study proposal, the preliminary Table of Contents and the Order Form, is available at: [http://www.catalystgrp.com/multiclient\\_studies/progress-in-technology-for-polyolefins-production-iii/](http://www.catalystgrp.com/multiclient_studies/progress-in-technology-for-polyolefins-production-iii/) or by contacting John J. Murphy at +1.215.628.4447 or [John.J.Murphy@catalystgrp.com](mailto:John.J.Murphy@catalystgrp.com).

