



## Review Article

# Technologies and Measures for Increasing Gasoline Production

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**Abstract:** As an important fuel energy source, gasoline plays a very important role in the national economy development of our country. Gasoline production increasing is a primary mission for petrochemical enterprises at present and even over a long period in the future to optimize production operation plan, adjust product slate, meet market demand and improve economic performance. This paper deeply analyzes and identifies gasoline production increasing potential of enterprises based on the practical production operation of C Company, considering the development progress and industrialized application of alkylation technology, isomerization technology, etherification technology, MTBE technology, residue hydrogenation technology, catalytic cracking and LCO hydro-upgrading-catalytic cracking combination technology at home and abroad. Additionally, this paper proposes constructive solutions for enterprises to further increase the production of gasoline, reduce diesel-gasoline ratio, optimize product slate, tap potentiality and increase efficiency and provides a reference for petroleum and petrochemical enterprises to establish slate adjustment development plan, on the basis of the long-term development plan of enterprises, aiming at “comprehensive utilization of resources by refining-chemical integration, increase gasoline blending components, increase the production of automobile gasoline and optimize product slate”, in the aspects of “plant operation scheme, catalyst grading scheme, production and processing scheme, plant slate adjustment and plant general process design”, etc.

**Keywords:** Increasing Gasoline Production, LTAG, FDFCC, FD2G, RLG, Alkylation, Isomerization, Etherification

## 1. Introduction

In recent years, with the popularization of family cars, the consumption of gasoline in domestic market has increased significantly. Refineries reduce diesel-gasoline ratio by adjusting product slate, mainly with the following measures: enhance the application of new technologies and new catalysts; modify and optimize stock assets; optimize the production scheme and operation parameters of refinery, etc. According to statistics, the average diesel-gasoline ratio of C Company was 1.45, 1.30 and 1.19 in 2014, 2015 and 2016 respectively. It is estimated that the ratio of diesel oil and gasoline consumed in domestic market will be reduced to 1.13 by 2020, and further reduced to 1.03 by 2025. This means a great pressure in increasing gasoline production.

## 2. Potential of Increasing Gasoline Production

### 2.1. Increasing Gasoline Production with $C_4$ - $C_6$ Resources

In the standard exposure draft of gasoline meeting China VI emission standard (China VI gasoline), olefins in gasoline are restricted below 15% vol., aromatics are restricted below 35% vol., benzene is restricted below 0.8% vol. and the 50% distil-off temperature of gasoline is restricted below 110°C. Alkylate, methyl tert-butyl ether (MTBE) and isomerized oil are gasoline blending components which are free of aromatics, olefins and benzene and characterized by a low 50% distil-off temperature. Except isomerized oil which has a high RVP (95-110 kPa), the other two components have a low vapor pressure, and are ideal gasoline blending components.

At present, C Company has two alkylation units in operation, with a capacity of approx 100 kt/a. If all after-etherification C4 resources of the company are converted into alkylate, the ratio of alkylate in gasoline pool of the company will be 7.5%, while the ratio of alkylate in gasoline pool of USA is 12.5% [1], so there is much room for increasing the production of alkylate.

MTBE capacity of C Company is approx 1 Mt/a. Since most of the isobutene component in FCC LPG of C Company has been used in the production of MTBE, to increase the production of MTBE, new technologies must be used to solve the problem of feedstock supply, e.g. produce propylene and MTBE by dehydrogenating propane and butane, produce propylene oxide and MTBE by isobutene + propylene cooxidation process, etc.

Some refineries lack of feedstock for producing MTBE and alkylate because their FCC LPG is sold. To upgrade gasoline quality, it can be considered to build an FCC light gasoline etherification unit. Light gasoline etherification can convert methanol into gasoline, which accounts 3.5% of FCC gasoline, while increasing light gasoline RON by 2 units and reducing the olefins in full range gasoline by 8-10% vol..

Isomerized oil can increase the front-end RON of gasoline and improve engine startability, and is a good gasoline blending component. The ratio of isomerized oil in gasoline pool is 6% for USA, approx 12% for Europe [1], and less than 0.02% for C Company. However the light hydrocarbon feed stocks of isomerized oil, including light naphtha (produced by atmospheric and vacuum distillation or hydrotreating), reforming topped oil, reforming pentane oil and hydrocracking light naphtha, have been used as gasoline blending components at present. So increasing the production of isomerized oil cannot increase the production of gasoline, but can increase the front-end RON of gasoline and reduce the 50% distil-off temperature.

## 2.2. Increasing Gasoline Production with Naphtha Resources

Since there are more and more ethylene plants using shale gas and oilfield associated gas as feedstock, it is estimated that part of naphtha resources will be used as a reforming feedstock rather than a steam cracking ethylene feedstock. Meanwhile, with the increasing demand of PX and jet fuel and the upgrade of automobile diesel oil, the capacity of hydrocracking will be increased gradually, with tail oil sent to ethylene plant to save part of naphtha for feeding reforming unit. The abovementioned factors will increase the available naphtha resources to allow the construction of CCR unit. Reformed gasoline is characterized by high aromatics, no olefins, low vapor pressure and high 50% distil-off temperature. At present, the content of aromatics in the gasoline pool of C Company is high, especially for high-grade gasoline. The volume fraction of aromatics is close to the upper limit of 35% in most refineries, and some refineries have to sell aromatics to have an acceptable content of aromatics. At present, no more reformed gasoline can be added into the gasoline pool until alkylate and MTBE are

added. It is estimated that up to approx 6.88 Mt/a reformed gasoline (with benzene removed) can be added, with a production increase potential of 12.3%.

## 2.3. Producing Gasoline with LCO

For LCO, which features high aromatics, high density and low cetane number, especially for MIP diesel oil with more than 70% aromatics and over 60% aromatics of two or more rings, simple hydrotreating or hydro-upgrading not only has a high hydrogen consumption but also can hardly have a cetane number meeting the standard of general diesel oils. See Figure 1 for LCO aromatics content varying with distillation range.

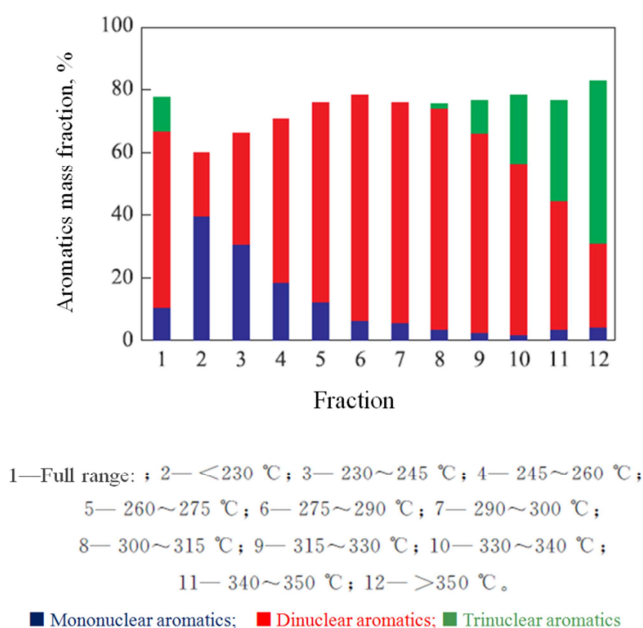


Figure 1. Distribution of Aromatics of LCO.

In recent years, it is an important R&D subject at home and abroad to make use of the high aromatics content of LCO to produce BTX (benzene, toluene, xylene) or high-RON gasoline blending components by hydrogenating aromatics of two or more rings into naphthene-aromatics and subsequent ring opening of naphthene. At present there are mainly 3 commercialized processes: (1) Hydrogenate LCO and recycle it to FCC unit to increase the production of gasoline; (2) Build an MP hydrocracking unit to process LCO separately and increase the production of high-aromatics and high-RON gasoline blending components; (3) Build an MP hydrocracking unit to produce BTX [2].

The FCC unit of C Company has a capacity of 70 Mt/a, with an average diesel oil yield of 22%, and annual production of 15 Mt LCO. Based on the surplus FCC capacity of 3.5 Mt/a, 2t LCO replacing 1t residual oil to feed FCC unit or 3t LCO replacing 1t gas oil to feed FCC unit, up to approx 5 Mt/a gasoline will be produced theoretically, with a production increase potential of 8.93%, and 9.1 Mt/a LCO will be consumed, accounting for 60% of the total amount, the rest 40% LCO will be used in the newly built MP hydrocracking unit to increase the production of gasoline,

with a production increase of approx 2.4 Mt/a and production increase potential of approx 4.29%.

To sum up, the potential of increasing gasoline production by increasing the production of alkylate, MTBE and reformed oil and LCO conversion is 28.42%. If the average annual growth rate of domestic gasoline consumption is 8%, the gasoline production demand can be only satisfied for 3-4 years in the future even with the maximum gasoline production increase potential. Obviously without additional capacity, there will be a great pressure in increasing gasoline production.

### 3. Technologies of Increasing Gasoline Production

#### 3.1. Alkylation Technology

Alkylation technology mainly includes liquid acid process and solid acid process. Liquid process includes hydrofluoric acid process, sulfuric acid process and ionic liquid process. Liquid acid alkylation process features high acid strength of catalyst, low reaction temperature, low pressure to maintain liquid phase reaction and high octane number of the produced alkylate. But solid acid process, due to its environment friendliness, is the research emphasis at present.

Composite ionic liquid alkylation (CILA) technology, with aluminum chlorate as catalyst, developed by China University of Petroleum, has been commercialized by a chemical company. Compared with sulfuric acid process alkylation technology, ionic liquid process has advantages of no acid regeneration, low investment and environment friendliness, and disadvantages such as high price of catalyst ionic liquid.

Solid acid alkylation process has advantages of no waste acid discharge, no pollution and no equipment corrosion, etc. during production, representing the development direction of alkylation technology. A 100 kt/a solid acid alkylation unit built by a refinery with Lummus technology has been put into operation. Sinopec Research Institute of Petroleum Processing (RIPP) is also developing solid acid alkylation technology independently, and now is carrying out industrial side stream test. Solid acid alkylation process, without product subsequent treatment and waste acid recovery, etc., requires lower equipment investment and maintenance cost than liquid acid process. However solid acid alkylation process has a severe requirement on feedstock, uses noble metal catalyst, and the catalyst must be regenerated frequently, so the catalyst cost and plant energy consumption are higher in comparison with liquid acid process.

For the sake of safety, USA and Europe no longer build new liquid acid process alkylation units, but seek for new alternative technologies, e.g. indirect alkylation process, solid acid alkylation process, ionic liquid process and butane oxidative dehydrogenation process [3].

Indirect alkylation [1, 4-5] involves isobutene dimerization to generate isooctene and isooctene hydrogenation to obtain isooctane [4]. Indirect alkylation unit can be built by modifying MTBE unit. Compared with direct alkylation

process, this process produces isooctane with higher RON and MON and lower RVP. Indirect alkylation technology uses mature solid acid polymerization catalyst, featuring environment friendly polymerization and hydrogenation, less total investment and higher product quality, its disadvantage is high hydrogen consumption.

#### 3.2. PO+MTBE Technology

Producing propylene oxide (PO) by isobutane and propylene cooxidation process with co-product MTBE is a technology for large scale production of MTBE at present. The licensors of this technology are Lyondell and Huntsman. Lyondell has 3 PO/TBA (tert-butyl alcohol) plants in the world, Huntsman has 1 plant in Port Neches, USA, with an annual capacity of 240 kt PO and 750 kt MTBE. In May 2017, a PO/MTBE plant of the same capacity jointly invested by a refinery under C Company and Huntsman was put into operation.

Isobutane and propylene cooxidation process has advantages of coproduction of PO and MTBE which are urgently needed in the market and widened sources of raw material for the production of MTBE and disadvantages of complicated process, high investment, large amount and difficult treatment of waste water and great demand for feedstock isobutane. Take C Company as an example, the throughput of FCC unit is 69.42 Mt in 2015, with average LPG yield of 17.8%, including 22wt% isobutane, and the total isobutane is only 2.72 Mt. Minus the isobutane consumed in alkylation, with all n-butane converted to isobutane, the total isobutane is only approx 1.40 Mt. So it is not practical for large scale construction of PO/MTBE plants. Coastal refineries can consider the construction of such plants by importing C<sub>4</sub> resources to meet the requirement of increasing MTBE production.

#### 3.3. Technology of Producing MTBE by Dehydrogenating Propane, Butane or Isobutane

The technology of producing propylene and MTBE by dehydrogenating mixed C<sub>3</sub> and C<sub>4</sub> alkanes or producing MTBE by dehydrogenating isobutane has been developed quickly in some refineries, mainly using Oleflex technology of UOP and Catofin technology of Lummus, with a capacity of 200-400 kt/a, investment of RMB 1-1.2 billion, and MTBE output of 160-350 kt/a.

Both technologies have been used in China, mostly Catofin technology. In comparison with PO/MTBE technology, the investment for dehydrogenation technology is low, but the demand for feedstock isobutane is great. To meet the feedstock supply, generally an n-butane isomerization unit is provided. Such plants can be constructed by coastal companies by importing C<sub>3</sub> and C<sub>4</sub> components or by regional refineries after concentrating C<sub>3</sub> and C<sub>4</sub> resources.

#### 3.4. CCR Technologies

SLCR and SCCR continuous reforming technologies of Sinopec Luoyang Petrochemical Engineering Corporation Ltd.

(LPEC) and Sinopec Engineering Incorporation (SEI) respectively have been commercialized. At present, in the 68 CCR units completed in China, 9 units use SLCR technology, and 2 use SCCC technology. The max. in-operation capacity for SLCR technology is 1.5 Mt/a, and the process package of 2.8 Mt/a has been developed. The max. in-operation capacity for SCCC technology is 1.0 Mt/a.

SLCR reforming reactors are stacked pairwise, SCCC reforming reactors are arranged separately in parallel. All reactors have the same size, catalyst loading ratio and space velocity, which allow easy design, manufacture, installation and maintenance and exchangeability of spares. SCCC catalyst is transferred in counter flow to allow a higher product yield and longer catalyst life. Both domestic CCR technologies have their own characteristics and are suitable for the construction of large-scale plants.

### 3.5. LCO To Aromatics and Gasoline Technology (LTAG)

In the diesel oil pool of China, light cycle oil (LCO)

accounts for approx 30%; in the diesel oil pool of C Company, LCO accounts for approx 21%. LCO features high content of sulfur, nitrogen and aromatics, high density and low cetane number. It is an effective way to use the high-content aromatics in LCO, especially dinuclear aromatics, to generate naphthene-aromatics by partial hydrogenation and saturation and then generate gasoline components with high-content monoaromatics by catalytic cracking reaction. RIPP has developed LTAG process based on this principle.

Figure 2 shows a schematic of LTAG process. The core of the process is optimizing the catalyst and operation parameters of hydrogenation unit to selectively hydrogenate dinuclear aromatics into naphthene-aromatics; optimizing the position of hydrogenated LCO entering riser, developing special cracking catalysts and selecting appropriate operation parameters (recycle ratio, catalyst-oil ratio) so that naphthene-aromatics are converted into monoaromatics by selective ring-opening cracking with less hydrogen transfer reactions.

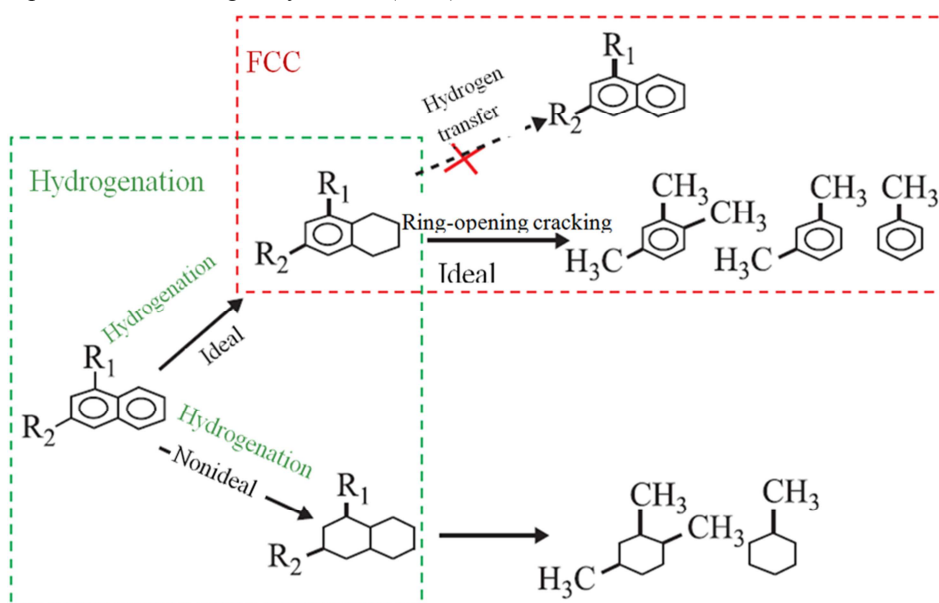


Figure 2. LTAG Process Schematic.

LTAG process includes two operating modes, i.e. hydrogenated LCO separate FCC mode and heavy oil blending hydrogenated LCO mode. With LTAG process, the gasoline product has higher aromatics and benzene contents and octane number, the LPG has lower isobutene content; the space velocity and severity of hydrogenation unit must be optimized to control the PAHs in refined diesel oil within a proper range.

### 3.6. Flexible Dual Riser Fluid Catalyst Cracking (FDFCC)

FDFCC is flexible dual riser fluid catalyst cracking process designed by LPEC. It was intended to increase the production of propylene and reduce the olefins and sulfur in gasoline, but not widely used due to its low gasoline yield and high energy consumption. However, pilot and commercial applications show that recycling hydrogenated LCO to FDFCC gasoline

riser renders a significant effect of LCO conversion to gasoline with a remarkable benefit.

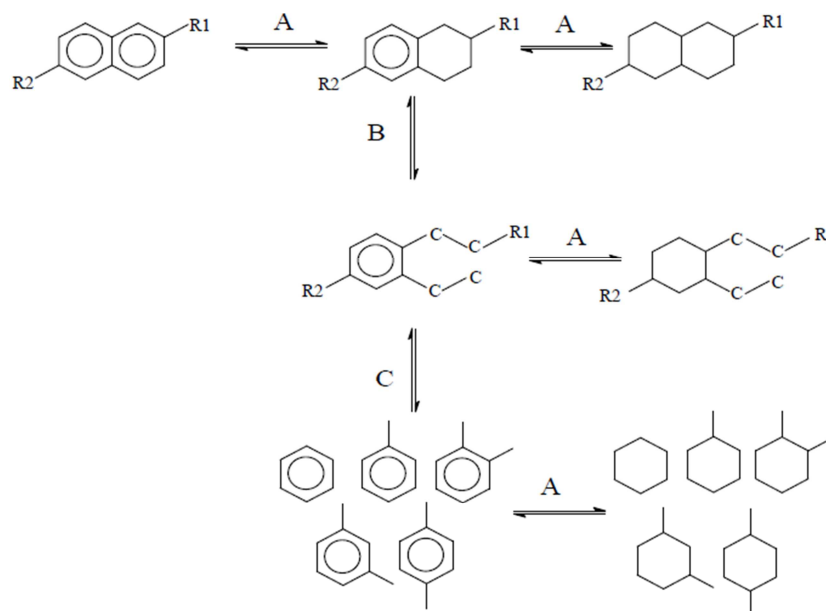
Different from LTAG process, the hydrogenated LCO is cracked separately, independent from heavy oil cracking. Within the allowable coke burning range of regenerator, the LCO handling capacity is high, and the reaction conditions can be adjusted in a wide range. Commercial applications show that the mass ratio of hydrogenated LCO feedstock/heavy oil feedstock can be greater than 0.5, and the specific gravity of hydrogenated LCO can be greater than 0.93, gasoline yield is higher than 53%, coking yield is lower than 4%, gasoline RON is higher than 96, olefins content is 6%, aromatics content is 40%-60%, benzene content is 1.5%. This process is suitable for recycling hydrogenated LCO. The LCO of refineries in a region can be collected, and an FDFCC unit can be built in, moved to or modified in a refinery for centralized processing of hydrogenated LCO.

### 3.7. LCO Hydrocracking Process (FD2G or RLG)

Sinopec Fushun Research Institute of Petroleum and Petrochemicals (FRIPP) and RIPP have developed FD2G and RLG LCO hydrocracking processes respectively. These processes are similar in principle and different in catalyst and

process parameters.

Figure 3 shows the schematic of these processes. The ideal reaction path is  $A \rightarrow B \rightarrow C$ , which features low hydrogen consumption and offers high-RON gasoline blending components.



A-Hydrogenation; B-Selective isomerization ring-opening cracking; C-Cracking (dealkylation)

**Figure 3.** LCO Hydrocracking Process Schematic.

Both processes require controlling hydrofining depth to improve ring-opening cracking ability. Therefore low-hydrogenation-activity highly acidic light oil type hydrocracking catalysts should be selected, and the reaction pressure should be controlled properly to inhibit aromatic saturation reaction under high pressure. Commercial applications show that during the early stage of operation, with the high hydrogenation activity of catalyst and low reaction temperature, the aromatic saturation degree and hydrogen consumption are high, and the gasoline yield and RON are low; during the final stage of operation, with the low hydrogenation activity and high reaction temperature, the aromatic saturation degree and hydrogen consumption are low, and the gasoline yield and RON are high. The hydrogenation activity of catalyst for such processes shall be reduced appropriately, and a high reaction temperature should be maintained.

### 3.8. $C_5/C_6$ Isomerization Technology

UOP keeps over 70% shares in  $C_5/C_6$  isomerization market, and owns 3 different isomerization technologies, i.e. Penex<sup>TM</sup>, Par-Isom<sup>TM</sup>, Hysomer<sup>TM</sup> [7], corresponding to low-temperature, medium-temperature and high-temperature processes, using catalyst carriers of  $AlCl_3$ ,  $ZrSO_4$  and molecular sieve respectively, with the same active component of Pt.

RIPP and East China University of Science and Technology have developed medium-temperature isomerization

technologies respectively, with catalyst active components of Pt and Pd respectively. The low-temperature and super acidic processes of RIPP are under commercialization test.

### 3.9. IHCC Technology

IHCC is an integrated catalytic cracking technology developed by RIPP, and has undergone commercialization test. Test result shows that IHCC process produces no slurry oil basically, reduces the yields of coke and dry gas significantly, increases gasoline yield from 42% to over 50%, with the yields of diesel oil and LPG basically unchanged or slightly reduced, aromatics in gasoline slightly reduced, olefins increased greatly, RON basically unchanged or slightly reduced, MON reduced by about 2 units. With the combination of IHCC technology and light gasoline etherification technology, the produced gasoline meets China VI emission standard.

### 3.10. Novel Catalytic Cracking Catalysts

Since 2000, the development of catalytic cracking technology has been mainly aimed at reducing olefins in gasoline, and catalysts have been designed with generally high hydrogen transfer activity, high level of rare earths, high content of molecular sieve, consideration of propylene production, high level of selective molecular sieve, consideration of blending in more residual oil, and high matrix activity [8]. The problem is, some plants over reduce olefins, resulting in low gasoline RON, high catalyst coking yield and



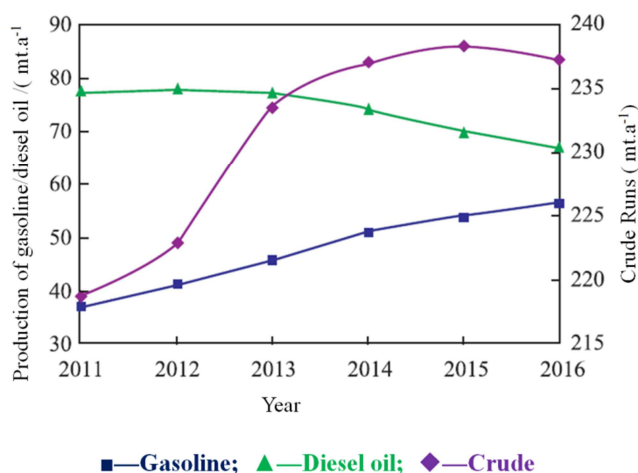
limited residual oil blending ability or handling capacity.

Now RIPP has developed ultra stable molecular sieves prepared by liquid phase fluorosilicic acid process and gas phase  $\text{SiCl}_4$  process, both of them have high B acids and low L acids to promote isomerization and cracking reaction, inhibit hydrogen transfer reaction and facilitate increasing gasoline RON and reducing coking selectivity. With the same conversion, gasoline RON is increased.

Although ultra stable molecular sieves can increase gasoline RON, they have disadvantages of poor hydrothermal stability and low activity. Now mesoporous molecular sieve is under development. This molecular sieve has hierarchical pores which facilitate increasing heavy oil cracking ability and reducing coking selectivity.

#### 4. Optimization Measures for Increasing Gasoline Production

Figure 4 shows the crude runs and gasoline/diesel oil production of C Company in recent years. As Figure 4 shows, the production of diesel oil peaked in 2013, and the crude runs peaked in 2015, while the production of gasoline has increased continuously. In 2016, C Company put into operation 11 LTAG revamp projects to increase the gasoline production by 1.2 Mt/a, nevertheless, the annual growth of total gasoline production is less than 2.5 Mt, and the growing is obviously slow. So measures should be taken to increase the production of gasoline.



**Figure 4.** Crude Runs and Gasoline/Diesel Oil Production of C Company in Recent Years.

##### 4.1. Increasing Production of Gasoline by FCC

FCC is the primary unit for increasing gasoline production, with measures to increase capacity mainly including debottleneck revamp, catalyst formula optimization, operation parameters optimization and feedstock optimization, etc.

The bottlenecks for capacity increasing are mostly in regeneration unit, e.g. inadequate main air, external heating capacity and coke burning degree, etc. Countermeasures include oxygen enrichment regeneration, additional external

heater, intensifying regeneration (e.g. adding grating of regenerator, increasing catalyst inventory, adding spent catalyst distributor, adding CO combustion improver), etc.

Catalyst formula optimization is also one of the main measures to increase gasoline RON. For example, for FCC units with hydrogenated gas oil as main feedstock, low- or no-rare earth ultra stable zeolite catalysts should be used, with low-content molecular sieve, inert matrix and single sol binder in the formula (silica sol has a better coke selectivity); for FCC units with small amount of residual oil blended in feedstock or feedstock subject to residual oil hydrogenation, ultra stable zeolite and low-rare earth zeolite composite catalyst should be used, with medium-content molecular sieve, medium-activity macropore matrix and double aluminum binder in the formula; for FCC units with large amount of residual oil blended in feedstock, ultra stable zeolite and medium-rare earth zeolite composite catalyst should be used, with high-content molecular sieve, rare-earth modified high-activity macropore matrix and double aluminum binder in the formula [8].

Optimization of operation parameters mainly includes the optimization of riser outlet temperature, catalyst-oil ratio, equilibrium catalyst activity, hydrogenated diesel oil recycle ratio, oil vapor partial pressure, FCC gasoline and diesel oil cut temperature and FCC gasoline vapor pressure, etc. To increase gasoline RON, FCC unit should operate at high temperature with appropriate catalyst-oil ratio and equilibrium catalyst activity and short contact time. Using top cycle oil instead of lean absorption oil can effectively increase the initial boiling point of LCO; properly reducing FCC gasoline vapor pressure allows more isomerized oil blended in gasoline pool. An additional online distillation range analyzer can be provided to monitor the distillation range of FCC gasoline; advanced process control system (APC) can realize stable boundary control of gasoline dry point to increase the production of gasoline. For the optimization of operation parameters, the conflict between economic benefit maximization and long-period operation must be balanced, giving attention to upstream-downstream integration and coordination optimization, e.g. residual oil hydrogenation-heavy oil FCC coordination optimization, FCC-delayed coking-gas oil/residual oil hydrogenation coordination optimization, FCC- LCO hydrogenation coordination optimization, etc. If FCC has a high conversion, then the LCO has a high density, the subsequent hydrogenation unit will have a high severity and high hydrogen consumption. Such operation parameters should not be optimized, and the severity of FCC should be reduced properly, this is also helpful to increase the processing load of FCC.

Developing feedstock sources and improving feedstock quality are also main measures to increase the production of gasoline by FCC. For example, vacuum deep cut revamp for atmospheric and vacuum distillation unit to hydrogenate heavy gas oil which was used as a feedstock of coker, and then use it as a feedstock of FCC unit to increase gasoline production and reduce diesel production; use straight-run heavy diesel oil or vacuum 1<sup>st</sup> side cut as a feedstock of FCC

unit to increase gasoline production; use coker gasoline as a feedstock of FCC unit to increase gasoline production; purchased gas oil, hydrocracking tail oil, atmospheric 1<sup>st</sup> side cut, hydrogenation recycled oil, hydrogenated diesel oil, pyrolysis C<sub>9</sub> gasoline and C<sub>9</sub>+ heavy aromatics, etc. can be used as feedstock of FCC unit, provided that closing monitoring is required to prevent coking.

#### 4.2. Increasing Production of Gasoline by CCR

Capacity increase of CCR units is generally restricted by reforming furnace load, regeneration coke burning capacity and pinning in reactor. The furnace load can be increased by adding furnace tubes and modifying burners, etc.; regeneration coke burning capacity can be improved by using low-coking rate catalyst, lengthening regenerator inner and outer meshes and extending coke burning area, etc.[9]. When the capacity is increased, the first reactor is subject to pinning, which can be prevented by connecting a crossover line from the inlet of the first reactor to the inlet of the second reactor. Some units are restricted by the load of plate exchanger which is also liable to leak, it can be replaced by spiral wounded heat exchanger.

Optimization of operation parameters mainly involves optimizing feed rate and operation severity. Traditionally it is believed that if the operation is as per gasoline slate, the optimization target is the maximum RON of reformed gasoline. According to the simulation result of kinetic model, with the current price system, the octane barrels of the oil produced by CCR peak at about 515°C, while the economic benefit peaks at 528-530°C. The preference of the two contrary sets of operation parameters, i.e. high capacity-low severity and low capacity-high severity, depends on the main process stream of the particular refinery and the particular product price. RSIM refinery simulation model is recommended for calculation and comparison.

With real-time online technology (RTO), the inlet temperature and hydrogen-oil ratio, etc. of 4 reactors can be tuned to increase gasoline production and maximize benefit. This technology has been used in some domestic refineries, and expected to be popularized gradually during the 13<sup>th</sup> Five-Year Plan.

With a high severity, some problems may occur during long period operation of CCR, some of them may force the reforming unit to reduce the operation severity and subsequently reduce gasoline production, e.g. high dry point and high gum content of the oil produced by reforming, frequent changing of gumbrine, high labor intensity and environmental pollution, etc. To solve the problem of high dry point and high gum content of the produced oil, a C<sub>9</sub>/C<sub>10</sub> separator can be provided after xylene column for gasoline blending with overheads and side cuts and diesel oil blending with bottoms. With the separator, the dry point of CCR feedstock can be increased to 172-174°C, the reaction temperature can be increased above 525°C; to solve the problem of frequent changing of gumbrine, non-hydrogen or hydrogen technology can be used to realize olefins saturation and greatly reduce the changing frequency of gumbrine or

even omit it.

For different crudes, the dry point of atmospheric and vacuum distillation primary tower overhead (primary overhead) naphtha and atmospheric tower overhead (atmospheric overhead) naphtha can be adjusted to feed primary overhead naphtha to steam cracking ethylene unit, and feed atmospheric naphtha to reforming unit. Now crude online analysis technology is mature, for different crudes, RTO technology can be used for online adjustment of the dry point of primary overhead naphtha and atmospheric overhead naphtha; with APC technology, the atmospheric overhead naphtha and atmospheric 1<sup>st</sup> side cut can be cut clearly to increase the production of reforming feedstock. UOP's MaxEne technology realizes adsorption separation of n-alkanes and iso-alkanes to feed n-alkanes to steam cracking ethylene unit, and feed other components to reforming unit.

#### 4.3. Reducing RON Loss of S Zorb and Gasoline Hydrogenation

S Zorb is a technology integrally purchased from ConocoPhillips and independently improved by Sinopec. Now it has developed to the third generation, with more than 20 plants and total capacity of 33 Mt/a, playing an important role in gasoline upgrading [10]. However at present there is about 2/3 S Zorb treated gasoline with sulfur mass fraction < 5 µg/g and about 14% S Zorb treated gasoline with sulfur mass fraction < 1 µg/g [11], the mass excess leads to unnecessary RON loss. It is mainly caused by excessive desulfurization, resulting in overreaction of olefins hydrogenation. To reduce RON loss, C Company mainly controls the activity of regenerable adsorbent, reaction temperature and hydrogen-oil ratio in stable control over feedstock processing capacity and feedstock quality, optimization of reaction operation parameters and optimization of regeneration operation parameters to reduce saturation reaction of olefins and reduce RON loss on the premise of ensuring acceptable sulfur content.

S Zorb reactor overhead filter differential pressure is a key parameter influencing the long-period operation of plant [12]. In production, the differential pressure rise rate is generally controlled by controlling reactor linear speed (0.35m/s) and the differential pressure between reactor bottom and reactor dilute phase.

The operation period of reactor overhead filter can also be extended by using domestic high-flux filter or more or longer filter elements to increase gasoline production.

To reduce RON loss, main optimization measures for gasoline hydrogenation unit are increasing the cut point of light gasoline and heavy gasoline and cutting clearly. When the cut point is increased, there will be more thiophenic sulfur in light gasoline, which must be removed by extraction, etc. Since olefins in gasoline are mostly on light end, when the cut point is increased, RON loss will be reduced. After clear cutting of light gasoline and heavy gasoline, light gasoline tailing will be mitigated, sulfur content will be reduced, so heavy gasoline hydrogenation severity will be reduced, and RON loss will be reduced.

#### 4.4. Optimizing Gasoline Blending Formula

After gasoline upgrading, the content of olefins and aromatics must be reduced significantly. It is estimated that the high RON and MON resources in gasoline pool will be reduced much, and more alkylate and MTBE must be blended in to meet quality requirement. The optimization direction of gasoline blending formula is to minimize the mass excess of product gasoline, e.g. RON and MON, etc, minimize the negative blending effect of RON and MON and increase economic benefit.

For C Company, FCC gasoline accounts for about 53% in blending pool, and has a high content of olefins, so MON is low; alkylate mainly consists of isoalkanes, and has high RON and MON. When alkylate is blended with FCC gasoline, the negative blending effect of MON is significant [13]. To reduce the negative blending effect of MON, reformed gasoline can be added. The aromatics in gasoline can inhibit the negative blending effect of alkylate MON.

MTBE has a positive effect when it is blended with FCC gasoline, reformed gasoline or alkylate [13]. At present, there is an increase room for the oxygen content in gasoline pool, and there will be more excessive oxygen when alkylate and isomerized oil are blended in. So MTBE component shall be blended in high grade gasoline preferably, while alkylate shall be minimized in low grade gasoline.

When gasoline is upgraded, the requirement on the content of olefins, aromatics and benzene is severer, and there are also restrictions of vapor pressure, oxygen content, RON, MON and sulfur content. In this context, gasoline blending is difficult, and it is necessary to provide online gasoline blending facilities to execute the optimized gasoline blending formula.

#### 4.5. Optimizing Plant Production Plan

##### 4.5.1. Optimizing Heavy Oil Processing Route, Deepening Heavy Oil Processing

Heavy oil processing route is significant to diesel/gasoline ratio. To reduce diesel/gasoline ratio, it is recommended to use "residual oil hydrogenation-heavy oil FCC" or "solvent deasphalting-DAO to gas (residual) oil hydrogenation-FCC" processing route, or "residual oil to coking-gas oil to FCC" processing route provided that vacuum deep cut is required, and coking shall operate at high temperature and low recycle ratio.

For residual oil hydrogenation, measures of optimizing catalyst grading, matching feedstock property with operation severity and reducing feedstock viscosity, etc can be taken to increase residue ratio and foreign material removing ability and extend operation period. A lead up-flow reactor can be provided to increase the capacity appropriately; a lead switchable guard reactor can be provided to extend operation period. For fixed bed residual oil hydrogenation unit, long-period operation problems mainly include reactor pressure drop rise, local hot spots and heat exchanger fouling, etc. Some units eliminated local hot spots and reduced radial temperature difference by modifying internals. Reactor

pressure drop rise is effectively controlled by optimizing demetallization agent and inhibitor types, optimizing injection position and injection rate and strengthening feedstock Fe and Ca content monitoring in upstream unit.

For heavy oil FCC, it is recommended to optimize product distribution on the basis of reducing coking selectivity and increasing residue blending capacity. Feedstock requirement varies with regeneration form. For feed stocks mainly consisting of hydrogenated residual oil, depending on the carbon residue and V content of the feedstock, counter-flow two-stage regeneration or front coke burning drum + 2-dense phase regeneration can be chosen. Commercial operation shows that the former is more adaptive to high-carbon residue and high V content feedstock and offers a high gasoline RON [14-15]. FCC settler coking is one of the major problems affecting the long-period operation of unit. At present, a great progress has been made in settler coking prevention technology, e.g. SEI VQS 2<sup>nd</sup> generation coking prevention technology used by Sinopec Shanghai Petrochemical Company Limited, which shows basically no coking in one cycle (4 years) of operation [16].

In C Company, refineries using "residual oil to coking - gas oil to FCC" processing route have common problems of low carbon residue in residual oil (< 20%) and high load of coking unit, etc. With vacuum deep cut revamp, these refineries can realize gasoline production increasing and diesel oil reducing. Refineries can also consider the construction of a solvent deasphalting unit. Now RIPP has developed the process package of 2.6 Mt/a large-scale solvent deasphalting unit. Vacuum residue undergoes solvent deasphalting, the deoiled asphalt (DOA) and the rest vacuum residue are fed to delayed coking unit, then DOA is fed to FCC unit, after gas oil hydrogenation or residual oil hydrogenation, to increase the production of gasoline. At present, the application of solvent deasphalting process is mainly restricted by the outlet of DOA, blending 30# asphalt with DOA [17] is a noteworthy subject. If slurry bed process with slurry oil, DOA and vacuum residue as feedstock can realize long-period commercialized operation, solvent deasphalting process will be developed rapidly.

For the optimization of delayed coking operation, the concept of "low-severity and long-coke-burning-period operation" should be changed to realize high-severity and short-coke-burning-period operation, e.g. increase furnace outlet temperature, reduce recycle ratio and reduce coking tower pressure, etc. At present, technologies of furnace wall burning, furnace tube online decoking, transfer line insulation, low recycle ratio and fractionating tower scrubbing section scrubbing effect increasing are mature, and can effectively solve the problems of coker gas oil (CGO) carrying fine coke, CGO carbon residue and high metal content, etc.

##### 4.5.2. Optimizing Gas Oil Processing Route

CGO has a high content of PAHs and nitrogen, when it is directly fed to FCC unit, the product distribution is poor. However if CGO is hydrogenated before feeding FCC unit, the gasoline yield will be increased significantly. Foreign



refineries generally hydrocrack CGO, some refineries of C Company also hydrocrack CGO. This scheme has a disadvantage, i.e. CGO carrying fine coke, which will increase the pressure drop of refining reactor and reduce the operation period. At present, some domestic hydrocrackers have their refining reactor loaded with nest form guard catalyst on the top, which effectively inhibits the rise of pressure drop.

The ex-factory price of FCC slurry oil is low or even negative. Before the filtering technology becoming mature, most refineries recycle the slurry oil to coker. Commercialized operation shows that CGO has a high content of aromatics and high density, even after processed in gas oil hydrogenation or residual oil hydrogenation unit, PAHs are hardly to saturate, and finally resulting in poor FCC product distribution, high coking rate, high yield of slurry oil and LCO, and low yield of gasoline. If the main process stream includes hydrocracking, some CGO can be fed to hydrocracker for ring opening of PAHs, which is helpful to reduce diesel-gasoline ratio. If the main process stream doesn't include hydrocracker, a slurry oil topping plant can be built, with heavy slurry oil used for producing asphalt modifier or blending asphalt, and light slurry oil fed to residual oil hydrocracker or directly fed to FCC unit. In some refineries, the FCC riser outlet temperature is high, the heavies in slurry oil are coked partially in coker and partially in FCC unit, this can also prevent the accumulation of heavy aromatics in CGO.

FCC recycle oil processing in residual oil hydrogenation unit can effectively reduce the viscosity, and subsequently reduce the pressure drop of feedstock filter, increase residual oil hydrotreating capacity, promote residual oil hydrofining reaction and inhibit asphaltene separation. The hydrogenated recycle oil is fed to FCC unit, with lower coking rate and slurry oil yield and higher liquid yield.

#### 4.5.3. Optimizing LCO Processing Route

At present, the practical operation of LTAG technology is subject to further summary and analysis. According to mass spectrometric data analysis, LCO fractions before 260°C contain more monoaromatics and less aromatics of two or more rings. Theoretically it is appropriate to feed LCO to FCC unit for recycling or to hydrocracker for producing heavy naphtha and jet fuel without hydrogenation, but for H LCO, due to its higher content of aromatics of two or more rings, hydrogenation before feeding FCC unit for recycling is appropriate. However, according to commercialized operation, LCO full range (with dry point below 360°C) hydrogenation before feeding FCC unit will reduce recycle ratio (mass ratio of hydrogenated LCO to FCC fresh feed), and more LCO must be discharged. Potential causes: 1. Low pressure rating of LCO hydrogenation unit of refinery, the partial pressure of hydrogen is lower than 7.0 MPa and hard to reduce the content of aromatics of two or more rings in LCO to 8%-10%; 2. After hydrogenated LCO recycling in FCC unit, some heavies are generated. In case of poor LCO hydrogenation, heavies of 330-360°C fraction will accumulate gradually till reaching a new balance. Therefore, the process of hydrogenated LCO recycling and HLCO hydrocracking for blending to prevent

accumulation of heavies in the system deserves a commercial test, and may have a good effect. For refineries without hydrocracker, it is recommended to feed HLCO and recycle oil together to residual oil hydrogenation unit to implement two-way combination process. For refineries with neither hydrocracker nor residual oil hydrogenation unit, HLCO can be used for marine fuel oil blending and regional mutual supply, etc. Some refineries also press HLCO into slurry oil, then feed it to delayed coker for recycling. The practice shows that there is no significant change to cetane number of CGO.

Some refineries send hydrogenated LCO to FDFCC unit gasoline riser for recycling, this can process not only all LCO produced by FDFCC unit but also external LCO, with a good effect.

After FD2G or RLG processing, whether the hydrogenated LCO is used for blending general diesel oil or sent to FCC unit for recycling requires economic analysis, and the process should be adjusted aiming at increasing economic benefit. LCO can also be sent to upgrading unit to produce high-potential-aromatics naphtha; or sent to hydrocracker for blending to produce heavy naphtha and jet fuel, but the smoke point of jet fuel and BMCI will be influenced slightly; or sent to residual oil hydrogenation unit to reduce feedstock viscosity and improve the stability of residual oil system.

It is predicted that 9 FCC units of C Company will complete LTAG technical transformation in 2017 to further increase gasoline capacity by 2.28 Mt/a. In two years 20 units will complete LTAG technical transformation to increase capacity of 3.48 Mt/a, accounting for 70% of conversion potential. In 2017, C Company will have 2 new RLG or FD2G units to increase gasoline capacity of approx 1 Mt/a.

#### 4.5.4. Optimizing Naphtha Processing Route

The refined naphtha produced by secondary processing units (e.g. residual oil hydrogenation, gas oil hydrogenation and LCO hydro-upgrading units, etc) has a high content of cyclanes and aromatics, and can be sent to CCR unit for processing. It is one of the measures to increase the production of CCR feedstock to build a light hydrocarbon recovery unit to cut light and heavy ends of straight run naphtha and secondary unit produced naphtha, use light naphtha as feedstock for steam cracking ethylene production and pre-hydrogenate heavy naphtha for reforming.

Refinery/chemical integrated refineries can realize steam cracking ethylene feedstock lightening and diversifying to effectively expand the sources of reforming feedstock. For example, ethylene-rich gas in dry gas of refineries can be recovered, hydrogenated and saturated dry coker gas and LPG can be used as cracking feedstock, more hydrocracking tail oil can be produced and used as cracking feedstock, and naphtha can be used as reformer feedstock, etc.

The ratio of methylcyclopentane and cyclohexane in hydrocracked naphtha is significantly higher than that in straight run naphtha, and the reformed methylcyclopentane is liable to generate cyclopentadiene, resulting in catalyst coking to reduce its activity and selectivity. So the initial boiling point of hydrocracked heavy naphtha shall be higher than 72°C.

Generally there is a high overlapping degree between hydrocracked jet fuel and heavy naphtha and between jet fuel and gas oil. The fractionating system should be revamped to increase the production of heavy naphtha and jet fuel while clearly cutting products.

#### 4.5.5. Optimizing Main Process Stream

For multiple fineries, the optimization of main process stream covers crude transportation optimization and regional resources optimization, etc. For one finery, the optimization of main process stream covers production plan optimization, scheme optimization and long-period operation optimization, etc.

Multiple refineries usually realize coordination benefits of reasonable utilization of resources, input reducing and output increasing, etc by enhancing concentration degree to realize the mutual supply of light hydrocarbons, hydrogen, LCO, naphtha, slurry oil and MTBE. Especially the mutual supply of light hydrocarbons, naphtha, MTBE and LCO has a significant positive effect on gasoline production increasing.

The main process stream optimization on refinery production plan must use computer model aided decision making, e.g. use PIMS model to fully consider the feedstock demand in refinery and chemical sectors, optimize crude category, processing capacity and plant production scheme (feedstock supply, processing load and product distribution) on the premise of ensuring the highest general benefit, determine the optimum production scheme and achieve the goal of gasoline production increasing.

The main process stream optimization on refinery short-term “deneckbottle” revamp should consider the weaknesses in the main process stream to improve plant protection and handling capacity, expand crude processing adaptability, expand hydrogen sources, reduce hydrogen cost and improve product quality, etc. Foreign refineries generally use PIMS planning model for sensibility analysis to identify “bottlenecks” of the main process stream, and carry out “debottleneck” revamp according to the importance and urgency.

The main process stream optimization on mid-long term planning determines the profitability of the refinery in the future, and is the key of refinery development. For example, crude adaptation revamp, low grade heavy oil deep processing and hydrogen resources comprehensive utilization, etc. Low grade heavy oil deep processing and hydrogen resources comprehensive utilization are important for mid-long term structure adjustment of refineries in the future. Studying slurry bed, boiling bed and solvent deasphalting combination technology to produce more gas oil and use it as FCC feedstock to produce gasoline and reduce coking capacity is probably the dominant heavy oil processing route in the future.

On operation, main process stream optimization requires identifying risks affecting long-period safe and smooth operation of plant, considering solutions in advance, enhancing the routine management of monitoring high-risks, key parts and weaknesses, and taking measures to eliminate

hidden production dangers in time. For example, enhance raw material management to ensure stable quality of materials; enhance process technology management to improve the stability of operation parameters and ensure reasonable alarm settings and effective interlocks; enhance process corrosion protection management and operation management to reduce unscheduled shutdowns; make use of big data analysis technology to realize the correlation analysis of abnormalities and failures and advance warning; enhance the management of APC operation to improve online operation effect.

The decision making department shall work out scientific and reasonable economic responsibility system evaluation methods, favoring the departments that sacrifice their own interests (energy consumption, chemical consumption and other operation indices) for increasing the overall efficiency to ensure the maximized overall benefit. On routine operation optimization, the main process stream optimization should use a severe plant model, e.g. RSIM model, to analyze the influence of production schemes, processing flows and operation parameters on plant benefit and gasoline production.

## 5. Conclusion

- (1) At present, C Company has a gasoline production increasing potential of 28.42%. In the near future, C Company will increase gasoline capacity by 7-8 Mt/a (accounting for approx 50% of total gasoline production increasing potential) by using technologies of LTAG, RLG or FD2G, alkylation, MTBE and light gasoline etherification, etc..
- (2) Appropriately building MTBE units in coastal refineries by optimally using self-produced and imported C<sub>4</sub> resources and new MTBE production technologies and properly increasing the ratio of MTBE in gasoline blending composition are effective measures for C Company to increase the production of gasoline.
- (3) LCO hydro-upgrading-catalytic cracking combination technology is effective to increase the production of gasoline, reduce diesel-gasoline ratio and optimize product slate. LCO hydrogenated by LTAG unit can increase gasoline production effectively by either separate processing in catalytic cracking unit or processing in gasoline lift pipe of FDFCC.
- (4) Heavy oil processing route is significant for reducing diesel oil, increasing gasoline and adjusting diesel-gasoline ratio. To increase gasoline production and reduce diesel/gasoline ratio, it is advisable to use “residual oil hydrogenation-heavy oil FCC” or “residual oil to coking-gas oil to FCC” processing route, provided that vacuum deep cut for crude oil unit and high temperature-low recycle ratio operation for coking are required.
- (5) Advanced process control (APC) and real-time online optimization (RTO) technologies allow fine control of plant operation and subsequently realize effective separation and precise control in the production of gasoline blending components in key units to increase

the production of gasoline blending components. Additionally, optimizing gasoline blending scheme and improving online gasoline blending facilities to realize precise blending are also important measures for increasing gasoline production.

- (6) To achieve the goal of maximizing gasoline production, it is necessary to comprehensively consider the material demand and relationship between refinery, aromatics and olefin units, research the status of available resources for gasoline blending components and optimize gasoline blending scheme in view of plant main process stream optimization, to realize the goal of maximizing gasoline production and the overall benefit.

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