

SOLUTIONS FOR UPGRADING GASOLINE PRODUCTS TO COMPLY WITH EURO V SPECIFICATIONS IN DUNG QUAT REFINERY

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<https://doi.org/10.47800/PVJ.2020.10-05>

Summary

Dung Quat refinery is under the management of Binh Son Refining and Petrochemical Joint Stock Company (BSR). Currently, Dung Quat refinery is facing opportunities and challenges from macroeconomic policies as well as the development trend of the oil and gas industry including the issue of improving product quality, enhancing operational efficiency and competitiveness to be able to survive and develop in a new situation.

In this article, the authors suggest solutions to upgrade Dung Quat refinery gasoline products to satisfy more stringent standards and environmental regulations. Standards here mean the Euro V standards set out in the EN 228:2008 applicable to gasoline/petrol respectively. Solutions proposed to overcome problems relate to benzene, sulfur and olefin content in BSR gasoline products.

The article proposes two basic solutions to upgrade the gasoline product quality of Dung Quat refinery with some preliminary estimates. Each solution has its own advantages and disadvantages. Depending on specific situations, the more suitable one will be selected. Detailed calculation will be performed if the product quality upgrading project is implemented.

Key words: Product quality upgrade, Euro V specifications, gasoline, Dung Quat refinery.

1. General information

Dung Quat refinery, the first oil refinery in Vietnam, started construction in 2005 and was officially put into operation in 2009. The Vietnam Oil and Gas Group (PVN) was assigned by the Vietnamese Government to proceed with construction investment in Dung Quat Industrial Zone, with a total design capacity of 6.5 million tons of crude oil (equivalent to 148,000 barrels per stream day, BPSD). Dung Quat refinery processes either 100% of Bach Ho crude oil or a mix of 85% of Bach Ho crude oil and 15% of Dubai crude oil [1]. Raw materials of Dung Quat refinery are quite diverse, including domestic crude oils from Bach Ho, Te Giac Trang, Su Tu Den, and Chim Sao, etc., and also other imported crude oils from Southeast Asia, America, Nigeria, Azerbaijan, and Russia, etc. The refinery can blend various types of crude oil together to form a mixture to feed into the Crude Distillation Unit (CDU). Depending on the calculation, evaluation, and plans of production and

procurement, etc., the specific ratio of crude oils will be adjusted to ensure technical constraints and economic benefit.

- Dung Quat refinery's products include [1]: Polypropylene (PP), LPG, Mogas RON 92 (M92), Mogas RON 95 (M95), Jet A1/kerosene, diesel oil (DO), fuel oil, and sulfur.

- Products of the refinery are mainly consumed domestically.

This article deals with the specification issue of sulfur benzene and olefin, which is regarded as a gasoline product. Therefore, the analysis and evaluation are mainly related to gasoline products. The refinery's M92 and M95 gasoline blends include [1]:

- + C4s: Mixed C4 from the gas plant;
- + Isomerase: Products from the Light Naphtha Isomerisation Unit (IZOM);
- + RFCC Naphtha: Naphtha from the Residue Fluid Catalytic Cracker (RFCC);



Date of receipt: 28/8/2020. Date of review and editing: 28/8 - 19/9/2020.
Date of approval: 21/9/2020.

+ Reformate: Products of CCR unit.

Recently, Dung Quat refinery is facing various opportunities and challenges resulted from macro-economic policies as well as current general trends in the petroleum sector and oil processing industry as shown in Figure 1.

Governments in the world have been mapping out roadmaps to meet the stringent requirements of fuel properties to reduce emissions, protect the health and quality of the air. Accordingly, Euro or equivalent standards will be used to assess fuel quality, emissions, and safety requirements. The European emission standards consist of Euro I, Euro II, Euro III, Euro IV, Euro V and Euro VI, which are different, from low to high, in some main properties such as sulfur content, olefin contents, aromatics and benzene contents. Vietnam has planned to apply Euro V for gasoline with maximum sulfur content of 10 ppm soon (2021 - 2022).

2. Analysis of gasoline product quality

Table 1 summarises the key parameters for current Dung Quat refinery gasoline products and the comparison with the Vietnam National Standard (as regulated in QCVN 1:2015/BKHCN) as well as with international quality standards (EN 228 for unleaded petrol).

In general, Dung Quat refinery gasoline product quality has some important characteristics as follows:

+ At present, Dung Quat refinery gasoline specifications adhere to Level 3 of gasoline standards stated in Vietnam National Standard QCVN 1:2015/BKHCN [3];

+ Compared to Euro V specifications, the quality of Dung Quat refinery gasoline products do not satisfy the following requirements: Total sulfur content (ppm wt.%), aromatic content (vol%), and olefin content (vol%).

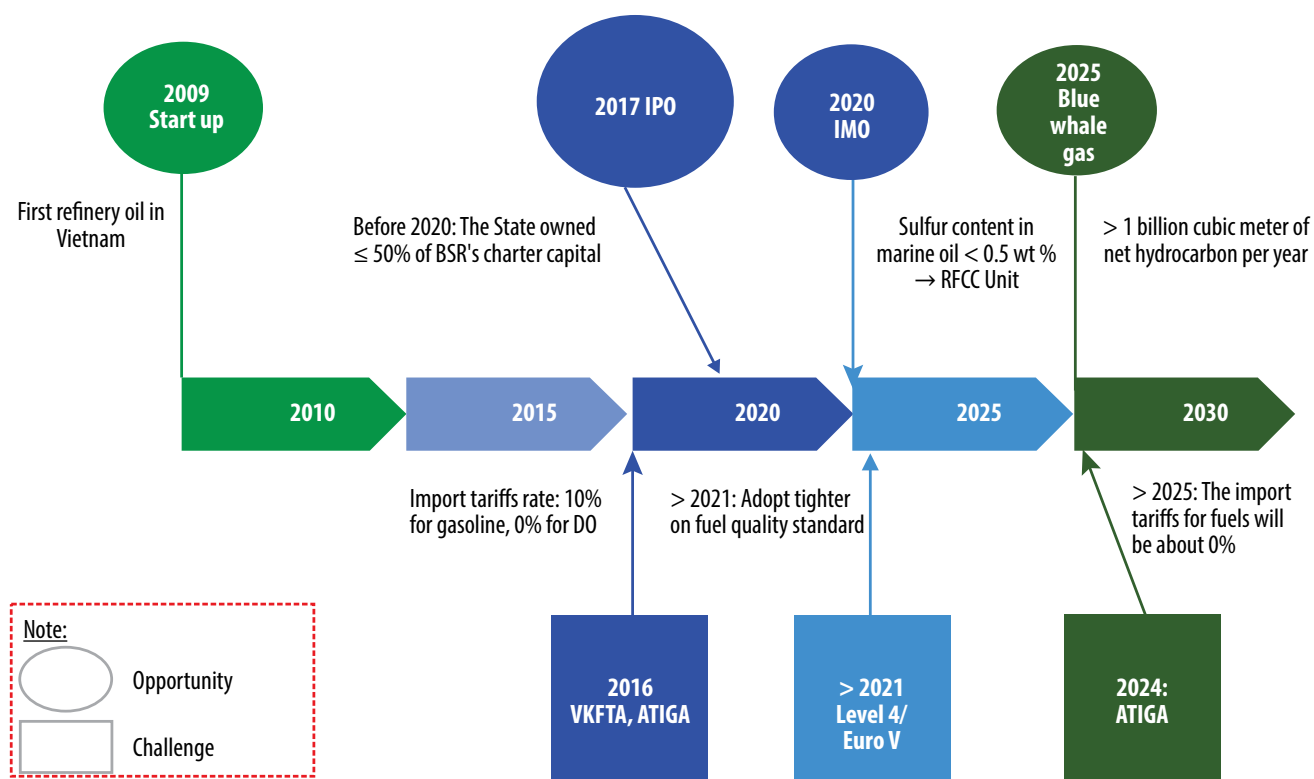


Figure 1. Opportunities and challenges for BSR.

Table 1. Important specifications of Dung Quat refinery gasoline products compared to standards [2, 3]

No.	Specification	M92			M95			Level 3 (QCVN, 2015)	Level 4 (QCVN, 2015)	Euro V/Level 5 (QCVN, draft version, 2020)
		Actual value								
		Min.	Average	Max.	Min.	Average	Max.			
1	RON	92	92.1	92.4	95	95.2	95.5	Min. 92/95	Min. 92/95	Min. 92/95
2	Total sulfur content (ppm wt.)	16	39	95	15	31	95	≤ 150	≤ 50	≤ 10
3	Benzene (vol%)	0.78	1.1	1.87	1.3	2.1	2.47	≤ 2.5	≤ 1	≤ 1
4	Olefin content (vol%)	28.9	34.4	38	21.6	30	36	≤ 30	≤ 30	≤ 18
5	Aromatic (vol %)	19.3	19.6	20.2	30	31.6	35	≤ 40	≤ 40	≤ 35

Therefore, with the goal of blending gasolines to meet Euro V specifications and ensuring that all produced components are blended, a technical solution should be considered.

3. Technical solutions to upgrade gasoline product quality

As aforementioned, in order to meet Euro V specification, the sulfur, benzene and olefin contents of Dung Quat refinery gasoline must be reduced. Technical solutions are considered as follows.

3.1. Solutions for reducing total sulfur content of gasoline products

According to the Dung Quat refinery gasoline product analysis data in 2017, the sulfur content in gasoline normally ranges from 39 ppm wt. to over 150 ppm wt., depending mainly on crude oil quality and technology parameters. Among the gasoline components, RFCC naphtha has the highest sulfur content, which results in its most considerable effect on the sulfur content of gasoline products. Other components such as reformate, isomate, and C4 mixture have lower sulfur content (less than 10 ppm wt.). Therefore, in order to reduce sulfur content of the commercial gasoline, it is necessary to deeply treat sulfur content of RFCC naphtha. Presently, RFCC naphtha is still being processed by the RFCC Naphtha Treating Unit (NTU) (Merichem's Technology) without using catalysts, so the treatment is hardly to decrease the sulfur content down to the required level (lower than 10 ppm wt.). Thus,

it is necessary to invest in a new treating unit to handle sulfur content of RFCC naphtha. Then, the sulfur content of final gasoline products will meet the target of less than 10 ppm wt. According to the 2016 production plan, the RFCC naphtha would reach the highest flow rate of about 43,000 BPSD when the plant was running at 105% of design capacity. In this project, if Dung Quat refinery runs at 115% capacity, the RFCC naphtha output will reach 47,000 BPSD roughly. For more flexibility in many cases, it is necessary to invest in a new treating unit with design capacity of about 50,000 BPSD.

Gasoline Hydrotreating Technology (GHDT) and GTC Technology are proposed in the article to upgrade RFCC naphtha. GHDT uses hydrogen and catalysts for reducing both sulfur and olefin contents in RFCC naphtha. However, GHDT technology also reduces RON of its products. By controlling the relation of olefin content and RON reduction in operation based on the range of technical design, it can harmonise RON and olefin content for gasoline blending to meet Euro V standards. Thus, GHDT technology can be a suitable technical solution to upgrade gasoline quality for Dung Quat refinery.

There are many GHDT licensors in the world such as UOP, Axens, and Haldor Topsoe, etc. Each technology has its own advantages and disadvantages. In this article, the database of a similar GHDT unit has been used to calculate. The detailed technology and licensor will be selected by the next steps if the upgrading project is carried out.

The process diagram of GHDT is shown in Figure 2.

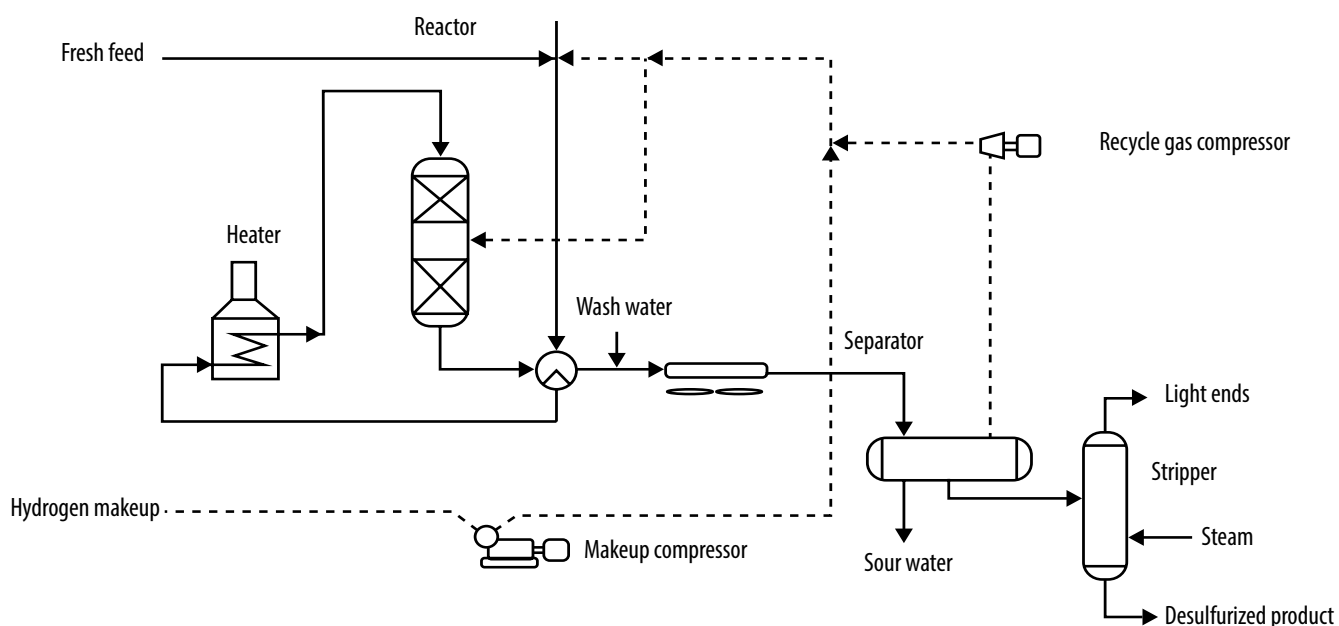


Figure 2. The general process scheme of GHDT unit [4].

GHDT products ensure sulfur content is lower than 10 ppm wt., satisfying Euro V specifications. However, there is also a disadvantage that after processing sulfur, it also reduces RON.

Another solution to be considered is the GTC's technology (GTC-BTX-Plus). RFCC naphtha stream flows into the existing NTU. Then, the NTU output stream is separated by 3 segments, including:

- RFCC light naphtha (C5 - C6') (LCN) to gasoline blending;
- RFCC medium naphtha (70 - 150 °C) (MCN) flows to sulfur and aromatic extraction module (solvent extraction technology). The aromatic stream with high RON is then treated with HDS module before going to the gasoline pool. The aromatic extracted MCN comes to the gasoline pool.
- RFCC heavy naphtha (>150 °C) (HCN) is also sent to HDS module to decrease sulfur and olefin content before coming to the gasoline pool.

In comparison to traditional gasoline hydrotreating unit, by separating naphtha by three fractions, GTC technology will minimise the octane loss due to olefin saturation reaction, which in turn limits the reduction of naphtha RON. The GTC unit will also reduce hydrogen consumption in the HDT module. By experience, the hydrogen consumption could even reduce by about 50%. It is very important because there is no hydrogen manufacture plant in Dung Quat refinery. However, GTC

technology requires adding a solvent extraction unit and the products have higher olefin content than those treated by GHDT.

The GTC general process scheme is presented in Figure 3.

3.2. Solutions for olefin content of gasoline products

According to the analysis of gasoline products, the olefin content of Dung Quat refinery Mogas 92 gasoline is often much higher than that of Mogas 95 (olefin in Mogas 92 is usually >30 vol%). The reason is that the composition of RFCC naphtha (the highest olefin components) occupies a large proportion in Mogas 92. Olefin content of Mogas 95 is typically less than 30 vol%, lower than stated in Euro V specifications. The olefin contents of other components (C4s, isomate, reformate) are lower than 30 vol%.

Therefore, it is necessary to have a solution. The solution will basically focus on RFCC naphtha, which is the component of the highest olefin content (about 40 - 50+ vol%). GHDT can reduce both sulfur and olefin content of RFCC naphtha to less than 30 vol%. Olefin reduction causes RON decrease, which will be customised for each specific case to balance the olefin content and RON of RFCC naphtha. Besides, adjusting RFCC catalyst quality or adding additives can also diminish the olefin content in RFCC naphtha.

GTC also has HDS modules. The whole or a part of HCN stream enters HDS module to lessen olefin content.

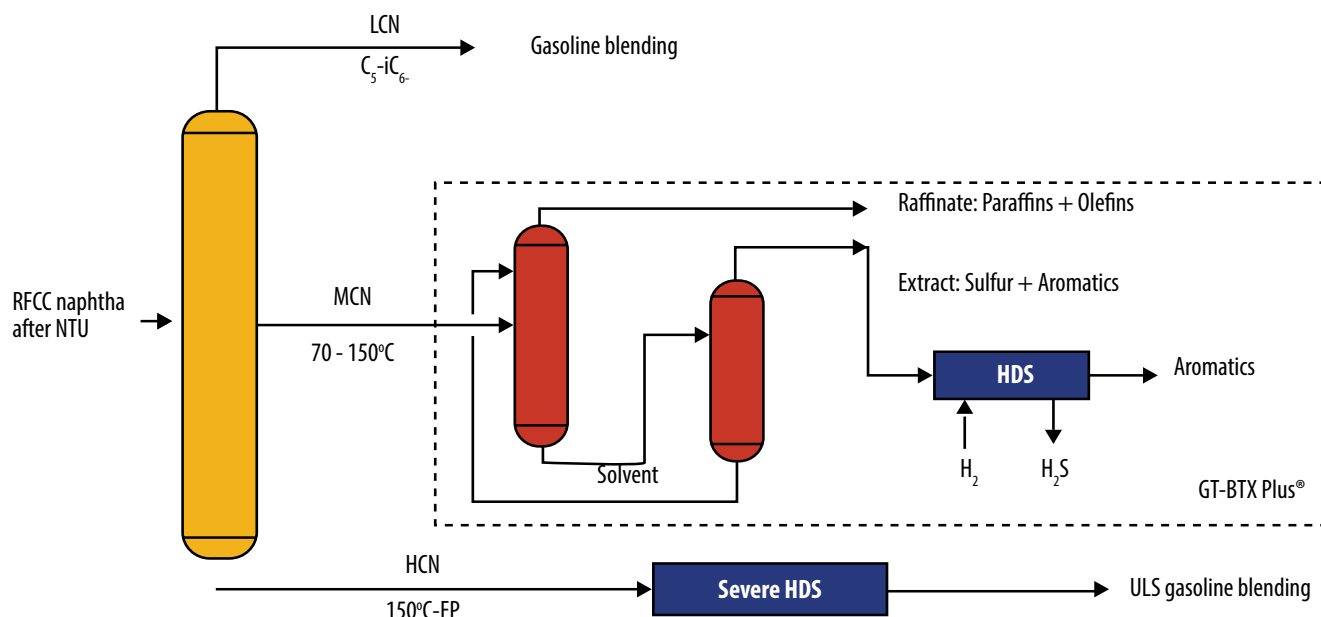


Figure 3. General process scheme of GTC unit [5].

3.3. Solutions for benzene content of gasoline products

In terms of technological configuration, the full range naphtha stream from CDU was passed through a naphtha hydrotreater (NHT) to remove sulfur and nitrogen, etc., then put into the naphtha splitter. The naphtha splitter is responsible for separating the treated full range naphtha stream into two fractions:

- + Light naphtha segment (LN) is used as raw material for IZOM;

- + Heavy naphtha segment (HN) is used as raw material for CCR.

Adjusting the operating parameters of naphtha splitter can affect the benzene and benzene precursor composition in LN and HN depending on single case. Benzene content in gasoline products is mostly from reformat (commonly 4 - 6 vol%). RFCC naphtha also has benzene content of less than 1 vol%. Most C_4 mixture and isomerate do not contain benzene. The refinery's M92 meets Level 2 of QCVN standard and the M95 meets the Euro 3 standard equivalent. The mandatory standard for benzene content of gasoline of the refinery is up to 2.5 vol%. According to the market demand, M95 gasoline consumption is quite large. Usually, the M95's price is higher than M92's.

In the current situation, the refinery's gasoline has a benzene content of ≤ 2.5 vol%, equivalent to Level 3 of QCVN [3]. M95 gasoline has an average benzene content of about 2.1 vol%. The reason is that M95 has a high composition of reformat components.

Considering the improvement of the refinery's gasoline quality to meet Euro V standards, according to the calculations, if the benzene content in reformat is not more than 2 vol% (safe level), then the complete blend

of the gasoline will meet the benzene requirement (≤ 1 vol%). Based on the collected data, normally the content of benzene and benzene precursor in the HN segment is about 4 - 6 vol% and similar in reformat (benzene is hardly converted through CCR). Therefore, it is possible to change the amount of C6 from HN segment into LN segment to ensure that the benzene content in the reformat will be no more than 2 vol%. However, due to the capacity and benzene content limitation of IZOM feed ($\leq 5 - 6$ vol%), if moving C6 into IZOM feedstock without other solutions, some problems in operation will arise, especially when using the crudes that have high yield of LN as well as C6 content.

Considering the current situation, the standard for gasoline's benzene content of the refinery is ≤ 2.5 vol%, the adjustment of C6 to LN/HN at naphtha splitter is much easier and more flexible. However, if moving most C6 to LN and feeding to IZOM, the whole RON will be lost because of benzene saturation. If C6 is moved to HN, the benzene content in reformat will be high and thus will affect the gasoline blending, especially M95. This will lead to a reduction in M95 gasoline blending because of benzene content constraint.

Thus, the following solutions for optimising the benzene content in the gasoline components should be considered.

- Adding C6 into LN to saturate and reduce benzene in gasoline:

Currently, IZOM can run up to 150% of design capacity. According to calculations, if cutting most C6 into IZOM, the unit will operate at 145 - 150% of the design capacity and IZOM can still handle it. There are advantage and disadvantage of this solution as follows:

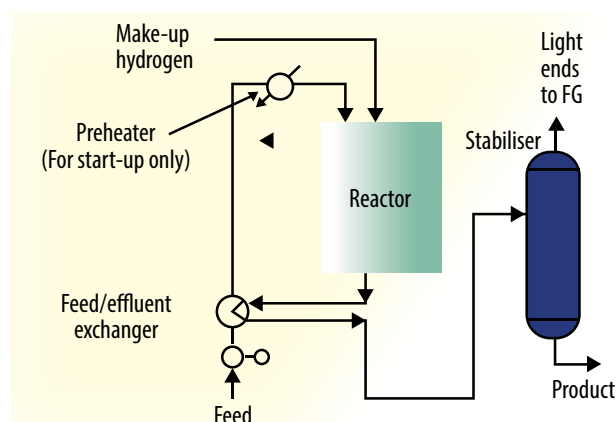
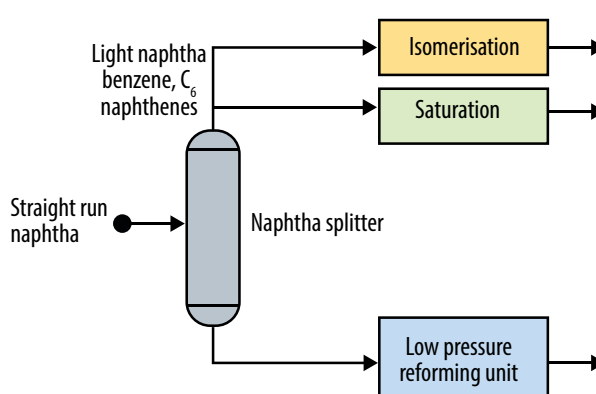


Figure 4. The general process diagram of BSU [6].



+ Advantage: No additional investment is required to reduce the benzene content in gasoline products;

+ Disadvantage: The benzene content of IZOM feedstock is required not to exceed 6 vol%. Therefore, if transferring too much C6 into LN and exceeding the limit of IZOM feed requirement, the performance of the unit will be affected. In addition, if the flowrate of LN is high, the unit will be overloaded. On the other hand, IZOM saturates benzene and causes RON reduction in the gasoline blending component.

- Investing in a new Benzene Saturation Unit (BSU):

BSU is responsible for benzene saturating in the LN fraction. The benzene content of the BSU product can be reduced to below 0.62 vol%. Investment cost is about USD 12 million for a capacity of 15,000 BPSD [6].

The general process diagram of BSU is shown in Figure 4.

+ Advantage: More benzene and benzene precursor can be added to the LN fraction to reduce benzene content of the CCR reformate. BSU can solve the benzene problem as well as the IZOM capacity limitation, especially in the case where crude oil feed or full range naphtha has a high yield of LN segment that is over IZOM's capacity ability. This option increases flexibility with crude oil feeds and meets the requirements of product quality improvement roadmap.

+ Disadvantage: Investment is a must. BSU saturates benzene and causes the loss of RON in gasoline blending. BSU also consumes additional hydrogen.

- Investing a new BenzOUT™ unit

BenzOUT™ is a technology of ExxonMobil Licensor. The role of BenzOUT™ is to reduce the Benzene content of reformate in the case of change almost of C6 into the HN segment at naphtha splitter. BenzOUT™ unit will separate the light reformate segment in the total CCR reformate including benzene and other C6. Then, light reformate is fed into the BenzOUT™ reaction section. The

BenzOUT™ also consumes an amount of propylene to produce higher quality gasoline in a similar form of alkylation. Heavy reformate stream is sent to gasoline blending. According to the data from the licensor, the benzene content of the BenzOUT™ product is dropped to < 0.62% vol% [4]. Investment cost is about USD 19 million for a capacity of 5,578 BPSD [6].

The general technology diagram of the BenzOUT™ is presented in Figure 5.

Advantages and disadvantages of BenzOUT™ are as follows.

+ Advantage: BenzOUT™ unit separates light reformate from CCR reformate and send to the BenzOUT™ reaction system to combine with propylene with the goal of reducing benzene content in reformate. In addition, BenzOUT™ product is a high RON component (RON >110). It can increase the total RON of reformate after BenzOUT™ up from 1.5 - 3.0 [4] and will contribute to increase the M95 quantity. The solution also helps the flexibility of the refinery increase by diversifying crude oil feedstock and following the direction of continuously improving product quality in the future.

+ Disadvantage: Investment costs are required. BenzOUT™ consumes propylene.

After considering the related issues, BenzOUT™ investment is the most suitable for Dung Quat refinery to handle the benzene problem in gasoline product of the refinery. This solution is both in line with the direction of improving the quality of gasoline products to meet Euro V standards in the future as well as enhancing the flexibility and efficiency of the plant in many cases. Therefore, the plan of installing BenzOUT™ is selected for further evaluation for the next sections.

3.4. Other indirect solutions for upgrading gasoline products to meet Euro V specifications

In addition, other solutions such as investment of Alkylation, ETBE Unit, or importing ethanol, etc., can be considered to improve the gasoline product quality.

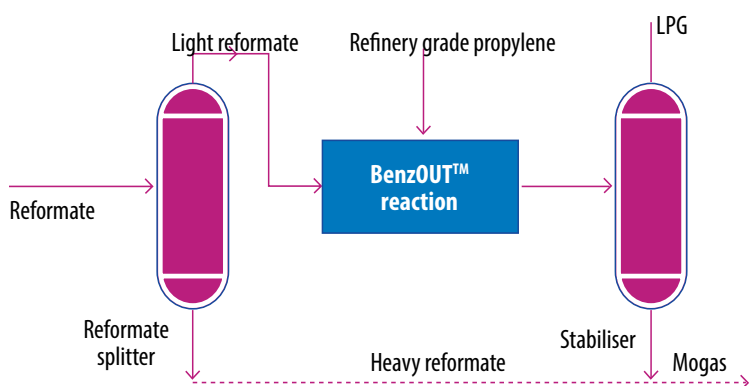


Figure 5. The general process diagram of BenzOUT™. Source: www.exxonmobilchemical.com [7].

4. The configuration of Dung Quat refinery before and after upgrading

In this article, the authors mainly use data from a project of VPI [8].

The existing general process flow diagram of Dung Quat refinery is shown in Figure 6.

There are 2 options studied in this article as follows:

- Option 1: Invest BenzOUT™, Alkylation and GHDT;
- Option 2: Invest BenzOUT™, Alkylation and GTC.

The Dung Quat refinery general process flow diagram for GHDT, BenzOUT™ and Alkylation (option 1) is proposed in Figure 7. Besides, a solution for diesel is also proposed in the scheme.

After installing BenzOUT™, GTC, and Alkylation (option 2), the general process diagram is described in Figure 8.

5. Comparison of key features between option 1 and option 2

Based on the data [8], the refinery capacity was at 110% of design capacity. The authors calculate the

overall material balance and operational efficiency of the refinery for 2 options by LP model. The product property constraints in the model are based on Euro V specifications. The process constraints refer to the current data of Dung Quat refinery's existing units. New units input data based on similar projects or technical documents [4, 5]. From the model calculation results, options 1 and 2 are compared in terms of the following:

- Operating/design capacity and investment cost;
- Typical properties of components and key specifications of gasoline products.

5.1. Capacity and preliminary investment cost estimation of new units for gasoline upgrade in 2 options

According to the calculation results, the operating capacity/design capacity and preliminary investment cost for gasoline upgrading of the new units are presented on Table 2. The existing units run within the limits of the allowed capacity.

As the data from Table 2, the investment cost of option 1 is higher than option 2. The cost will be calculated more precisely in the next steps.

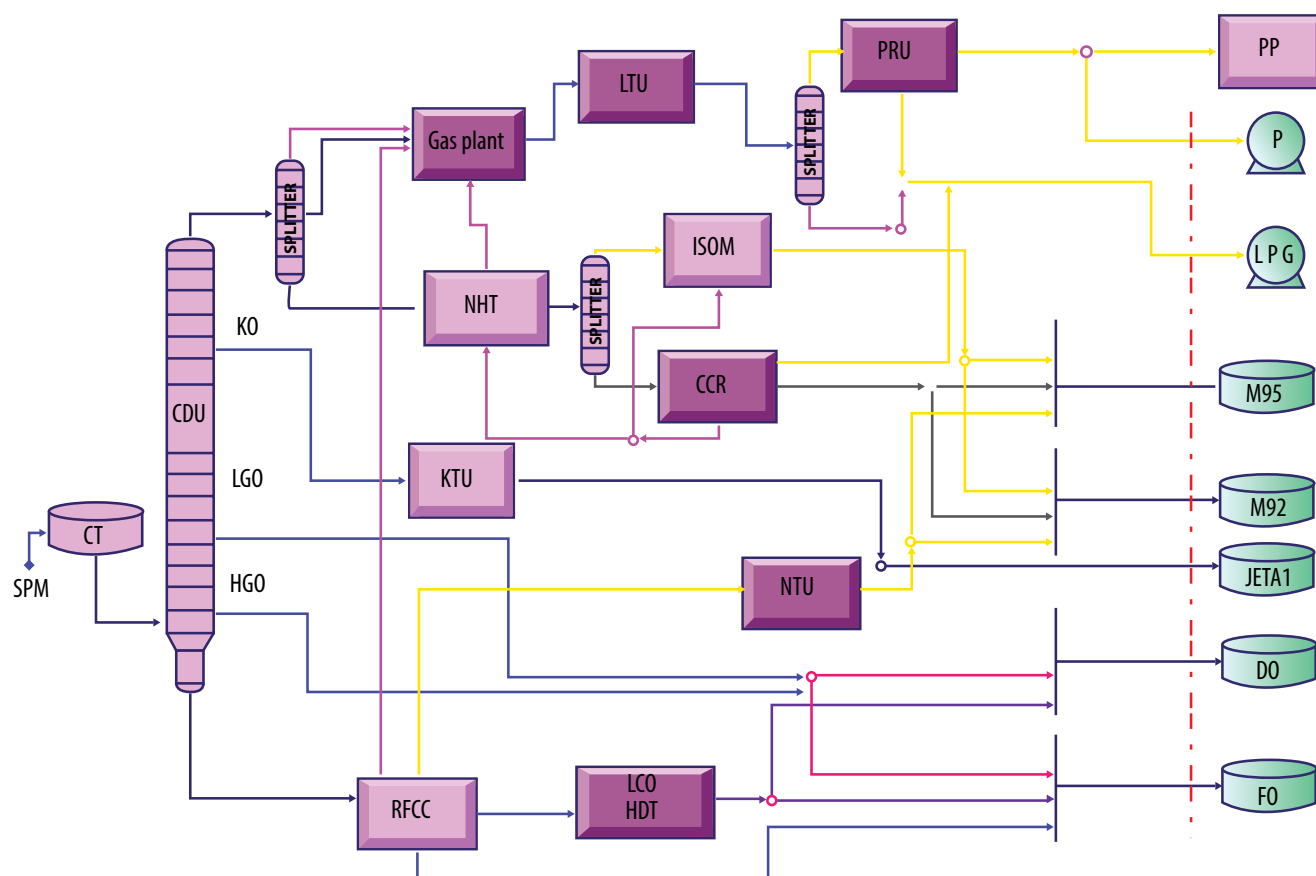


Figure 6. Existing general process flow diagram of Dung Quat refinery.

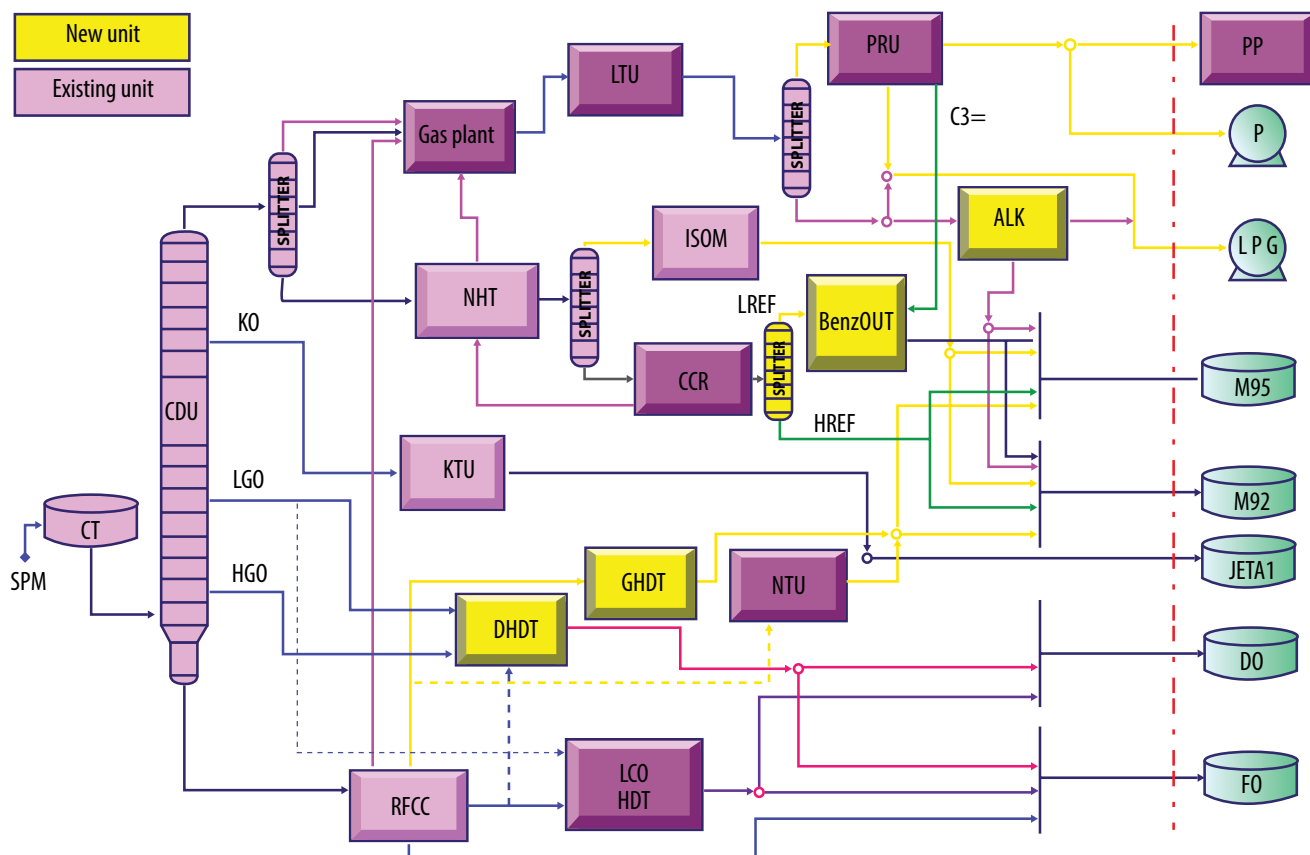


Figure 7. Dung Quat refinery general process flow after investing BenzOUT™, GHDT, Alkylation for upgrading gasoline quality to meet Euro V specifications.

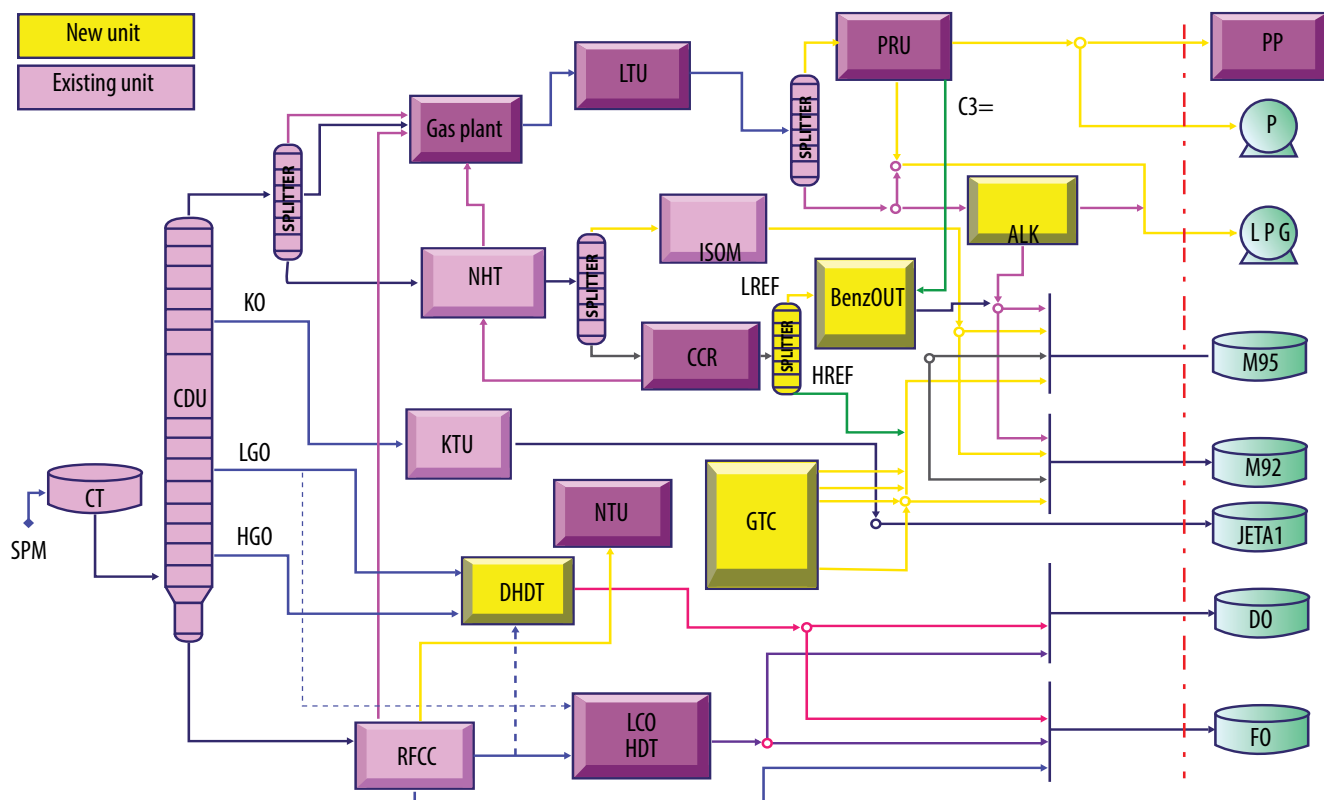


Figure 8. Dung Quat refinery general process flow after investing BenzOUT™, GTC, and Alkylation for upgrading gasoline quality to meet Euro V specifications.

Table 2. New units operating capacity, design capacity and preliminary investment cost estimation [4]

Unit	Description	Units operating capacity of option 1 (BPSD)	Units operating capacity of option 2 (BPSD)	New units design capacity (BPSD)	Preliminary estimated investment cost (MMUSD)	Remarks
GHDT	RFCC gasoline hydrotreating unit	45,335	-	50,000	89.9	10% margin of highest operating capacity in 2 options
ALK	Alkylation unit	10,864	10,214	11,950	35.4	10% margin of highest operating capacity in 2 options
BenzOUT™	BenzOUT™ unit	3,100	3,193	3,510	12.8	10% margin of highest operating capacity in 2 options
GTC	GTC unit	-	22,667	24,930	72.5	10% margin of highest operating capacity in 2 options
Estimated investment cost in option 1					138.1	
Estimated investment cost in option 2					120.7	

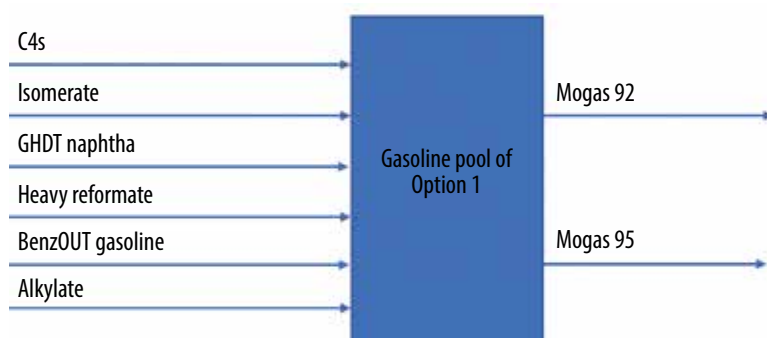


Figure 9. Simple gasoline blending sketch of option 1.

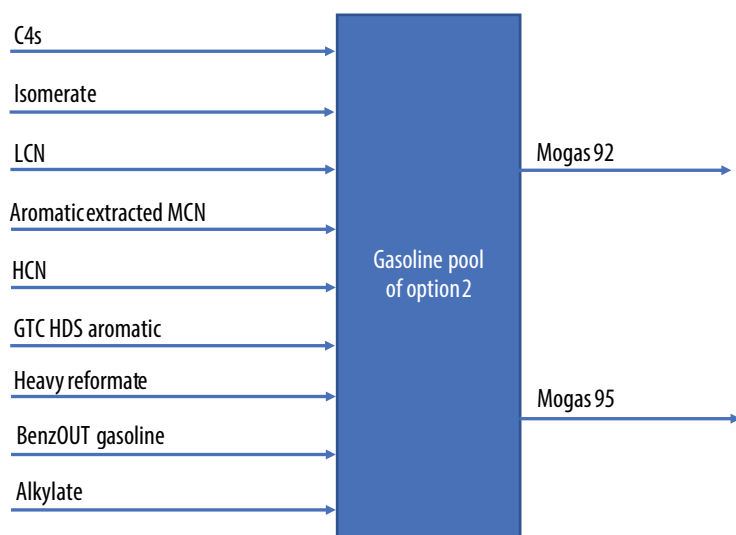


Figure 10. Simple gasoline blending sketch of option 2.

5.2. The typical properties and gasoline products' key specifications in 2 options

Gasoline components in 2 options appear in the following sketches. Gasoline blending sketch of option 1 is described in Figure 9. Figure 10 shows gasoline blending sketch of option 2.

Based on Figures 9 and 10, the number of components in option 2 (9 components) is more than the number in option 1 (6 components). Among them, there are 5 similar components: C4s, isomerate, heavy reformate, BenzOUT™ gasoline and alkylate. The main difference in the 2 options is GHDT/GTC technology. In the case of GTC, there are 4 components: LCN, aromatic extracted MCN, HCN, GTC HDS aromatic while only GHDT gasoline in the case of GHDT.

The advantages and disadvantages of GTC and GHDT are mentioned in Part III. There will be more suitable selections and considerations depending on the specific situations. This article mainly proposes solutions and does not concentrate in technology selection. It will be done in the next steps in case the project is implemented.

From calculation results, some typical properties and proportions of gasoline components in options 1 and 2 are presented in Tables 3 and 4.

The data in Tables 3 and 4 show that gasoline output in the 2 options is almost equal. The quantity of M95 in option 2 is slightly higher than in option 1. Gasoline products of the 2 options comply with Euro V specifications and Level 5 (QCVN, draft version, 2020).

The above is the preliminary calculation result. A more detailed assessment will be carried out in the next phases.

Table 3. Some typical properties and proportions of gasoline components in option 1

No.	Specification	Gasoline components						Gasoline products		Euro V	Level 5 (QCVN, draft version, 2020)
		C4s	Isomerate	GHDT gasoline	Heavy reformate	BenzOUT™ gasoline	Alkylate	M92	M95		
1	Vol% in M92	1.35	9.07	66.16	13.32	2.23	7.87	50,436 (BPSD)			
	Vol% in M95	2.15	6.21	45.91	20.74	6.06	18.93		24,892 (BPSD)		
2	RON	99.9	86.9	89.1	103.1	113.0	97.1	92.0	95.0	Min. 92/95	Min. 92/95
3	Total sulfur content (ppm wt.)	0	0	9.9	0	0	0	6.6	4.6	≤ 10	≤ 10
4	Benzene (vol%)	0	0	0.65	2	0.62	0	0.71	0.75	≤ 1.0	≤ 1.0
5	Olefin content (vol%)	22.5	0	24.5	1.5	0	0.5	16.4	11.91	≤ 18	≤ 18
6	Aromatic (vol%)	0	0	13.8	77.1	85.2	0	21.3	27.48	≤ 35	≤ 35

Table 4. Some typical properties and proportions of gasoline components in option 2

No.	Specification	Gasoline components										Gasoline products		Euro V	Level 5 (QCVN, draft version, 2020)
		C4s	Isomerate	LCN	Aromatic extracted MCN	HCN	GTC HDS aromatic	Heavy reformate	BenzOUT ^T gasoline	Alkylate	M92	M95			
1	Vol% in M92	1.28	8.93	19.66	24.63	11.48	3.53	17.99	2.00	10.51	49,967 (BPSD)				
	Vol% in M95	1.06	6.54	23.16	21.33	3.88	12.79	12.90	6.80	11.54		25,196 (BPSD)			
2	RON	99.9	86.9	91.0	87.0	78.0	104.8	103.1	113.0	97.1	92.0	95.0	Min. 92/95	Min. 92/95	
3	Total sulfur content (ppm wt.)	0	0	25	10	9	9	0	0	0	9.8	9.7	≤ 10	≤ 10	
4	Benzene (vol%)	0	0	0	0.8	0	1.4	2	0.62	0	0.61	0.62	≤ 1.0	≤ 1.0	
5	Olefin content (vol%)	22.5	0	39.2	34.5	5.8	0	1.5	0	0.5	17.53	17.21	≤ 18	≤ 18	
6	Aromatic (vol%)	0	0	2.5	2.4	3.2	98.2	77.1	85.2	0	20.26	29.27	≤ 35	≤ 35	

6. Conclusion

This article has analysed the issues and proposed two basic upgrade options for Dung Quat refinery gasoline products. Both solutions achieve the target of gasoline product quality reaching Euro V specifications with the investment cost estimated of about USD 140 million in option 1 and about USD 120 million in option 2. The difference between 2 options is that option 1 uses GHDT technology while option 2 uses GTC's technology to upgrade RFCC naphtha to reduce the sulfur content and olefin content. Both options use BenzOUT™ Technology, which not only reduces the benzene content but also increases RON of reformat. Besides, the authors also present alkylation investment to produce alkylate that is a high-quality gasoline component. Both options are compatible with the production of E5 gasoline to supply to the market when needed.

This article mostly uses input data from 2017 - 2018. The calculation is at a preliminary level. Detailed calculation and investment estimation of the solutions will be performed thoroughly in the next steps if the project is implemented.

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