GAS OIL COMPONENT AND THE EFFECTS OF THE CHANGING GAS OIL QUALITY REQUIREMENT*

by

A.S. Nasution and E. Jasjfi

ABSTRACT

The survey of gas oil production and impact of more stringent specification on the catalyst performance of ASEAN refineries conducted in 1996 revealed that a total feedstock of 5,673 MBPSD are processed into 1,131 MBPSD gas oil. This consists of the following product distribution: straight-run gas oil 85.44%, thermal cracked gas oil 2.52% cat. cracked gas oil 3.50% and hydrocracked gas oil 8.54 % on total gas oil products. About 50% of this total gas oil is processed in hydrotreating processes to improve the performance of diesel oil.

This paper reviews the production of gas oil components in ASEAN and the effect of the changing gas oil quality requirement on hydrotreating catalyst performance.

I. INTRODUCTION

Worldwide crude supply is experiencing a modest trend toward heavier and high sulfur content. The average annual demand growth rate for light products (gasoline, kerosene and diesel oil) is higher than that for residual fuel oil[1,2]

Gas oil components produced in the refineries generally consist of predominantly straight-run gas oil obtained from the fractional distillation of crude oil; however, compounds such as thermally and catalytically cracked gas oils are sometimes included.

The quality of straight-run gas oil, such as hydrocarbon. types, sulfur or wax content, will in general reflect the nature of crude oil. Naphthenic straight-run gas oil and cracked stocks, either thermal or catalytic cracked gas oil, contain higher percentage of aromatics than the paraffinic straight-run and hydrocracked gas oils. Sulfur content of gas oil components increase with the types of feedstocks.

The passage of the Clean Air Act Amendment of 1990 in the USA has forced American refineries to install new facilities to comply with stricter specifications for fuels such as gasoline and diesel oil. Current diesel specifications include a maximum sulfur content of 0.05 wt. %, a minimum cetane index of 40, and a maximum 10 vol.% aromatics[3,4,5]. For the even stricter diesel oil specification in the years 2000's, over 50% by volume of the total gas oil component (except hydrocracked gas oil) must undergo improvement by hydrotreating processes in order to achieve a suitable specification. With increasing cracked stock portion in the diesel oil pool and the stricter diesel oil specifications, the deep gas oil hydrotreating process will play a more important role[6].

This paper reviews tile production of gas oil components in ASEAN and the effect of the changing gas oil quality requirement on hydrotreating catalyst performance.

II. GAS OIL PRODUCTION IN ASEAN

Over 5,673 MBPSD of feedstocks is currently processed into 1,131 MBPSD gas oil products. This consists of the following product distribution: straight-run gas oil 85.44%, thermal cracked gas oil 2.52%, catalytic cracked gas oil 3.50% and hydrocracked gas oil 8.54% on the total gas oil products[7]

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About 50% on this total gas oil is hydrotreated to improve the performance of diesel oil[6].

The quality of straight-run gas oil, such as hydrocarbon types, Sulfur or wax content, will in general reflect the nature of the crude oil. Sulfur content of straight-run gas oil increase with the sulfur content of crude oil.

Cracked stocks, either thermal or catalytically cracked gas oil, contain higher percentage of aromatic and olefinic hydrocarbons than the straight-run gas oil. Gas oils from naphthenic crude oil (i.e. paraffinic straight-run and hydrocracked gas oils) have a higher specific gravity and a low pour point. Sulfur content of cracked stocks increases with their boiling range.

The influence of residual yield of atmospheric distilation processs, of coke yield of coking process, and of feedstock conversion of catalytic cracking and hydrocracking processses on the yields of the gas oil distillate products are given in the Figures 1, 2, 3 and 4, respectively. Relation between sulfur content of feedstocks and gas oil products is shown in the Figures 5. High specific gravity and aromatic content result in low performance diesel fuels. The relation between specific gravity and cetane number of gas oil is shown in Figure 6. Gas oil production of various processes and yield of gas oil produced on the feedstock used is given in the Figure 7.

The cetane number of these gas oils and automotive diesel oil blending components can be classified as follows:

- Low cetane number gas oils are naphthenic straight-run, thermal cracked and naphthenic catalytic cracked having cetane number between 25 to 35.
- Medium cetane number gas oils are intermediate straight-run and paraffinic catalytic cracked having cetane number between 40 to 50.
- High cetane number gas oils are paraffinic straight-run and hydrocracked having cetane number between. 55 to 70.

Some upgrading treatment may be needed if the proportion of the low performance of these non-paraffinic straight-run thermal and catalytic cracked gas

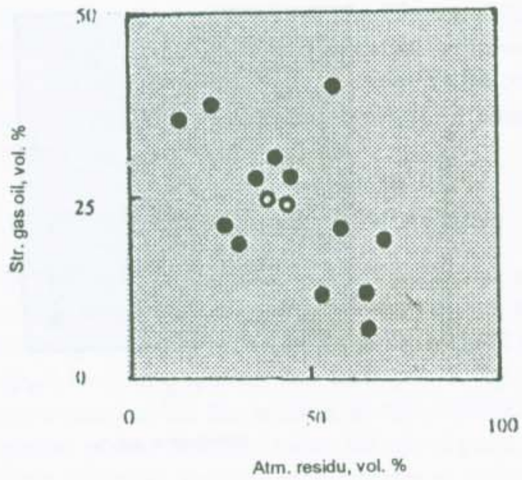


Figure 1
Relation between field of residue and gas oil product of atmospheric distillation process

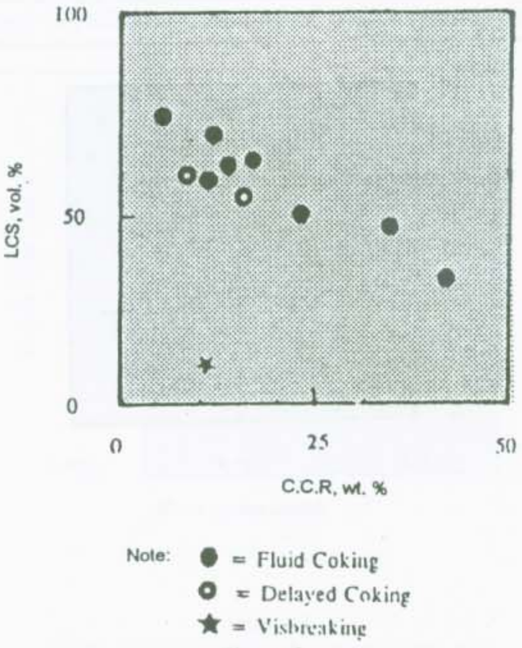


Figure 2
Relation between Conradson carbon residue of feedstock and yield of light cycle stock product of coking process

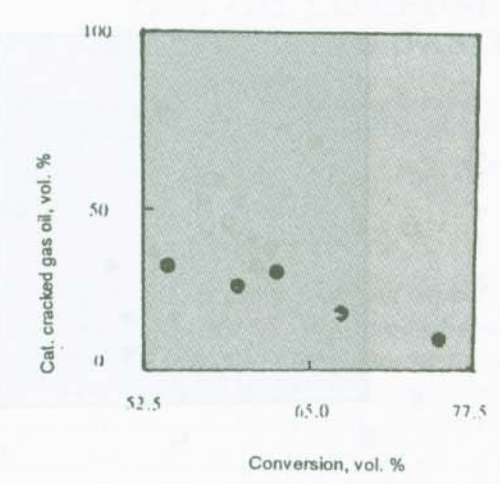


Figure 3
Relation between feedstock conversion and yield of gas oil product of cat cracking process

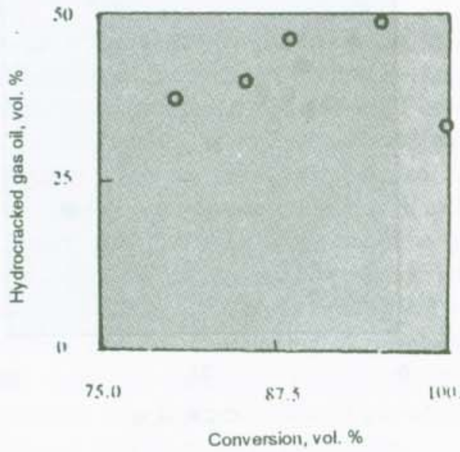


Figure 4
Relation between feedstock conversion and yield of gas product of hydrocracking process

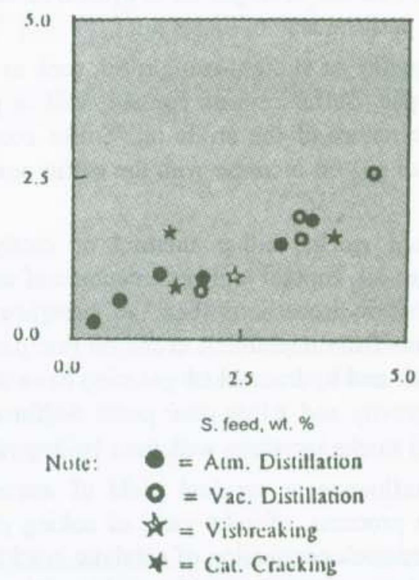


Figure 5
Relation between sulphur content of feedstock and gas oil products of several processes

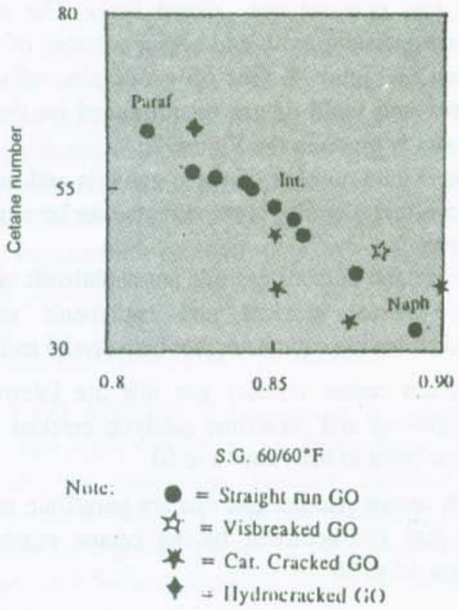


Figure 6
Relation between specific gravity and cetane number of gas oils

oils in the refinery gas oil/automotive diesel oil pool exceeds a certain value.

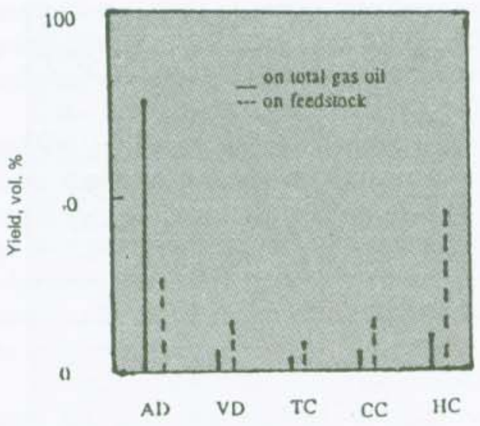
Catalytic hydrotreating processs reduces both sulfur and aromatic contents and improves colour and stability, as well as burning characteristics so that they meet the stringent specifications required for high performance gas oil and automotive diesel oil. Relation between operating pressure and sulfur content of hydrotreating gas oil is given in Figure 8.

The specific gravity in general increases by 1-4 API, with the more severe processing conditions utilized and the cracked stock gives the greatest increase. The copper strip test is good, and the extent of desulfurization is normally 70-95 %, with mercaptans being completely removed. The characterization factor increases approximately 0.2. In that case, hydrogenation causes a significant decrease in the boiling range of the cracked stocks. Carbon residue on the 10% bottom decreases to less than 0.1%. Neutralization value is reduced to 0.1% or less. Cetane number of both straight-run and cracked gas oil increase by 1-6 points[8,9]. This results in excellent quality with respect to improve performance of both gas oil and automotive diesel oil blending components. Thus, utilization of the catalytic hydrotreating processes plays an important role on the production of high performance of gas oil and automotive diesel oil blending components.

III. TRENDS IN GAS OIL SPECIFICATION

The flexibility of the refiner is seriously impaired by the interdependence of product properties, i.e. the ignition properties of gas oil and automotive diesel oil as defined by cetane number can be improved by removing aromatics, but the process, in turn, decreases the specific gravity and also raises the cloud point. It is evident, therefore, that the requirements of high ignition quality are in conflict with the demand for maximum economy and good low temperature operability.

It is clear that gas oil and automotive diesel oils are compromise products, and the fuel supplier has to engage in judicious blending of components in order



Note : AD = Atm. DistillationVD = Vac. Dist.
TC = Thermal Cracking
CC = Cat. Cracking
HC = Hydrocracking

Figure 7
Gas oil production of various process and yield of gas oil product on the feedstock used

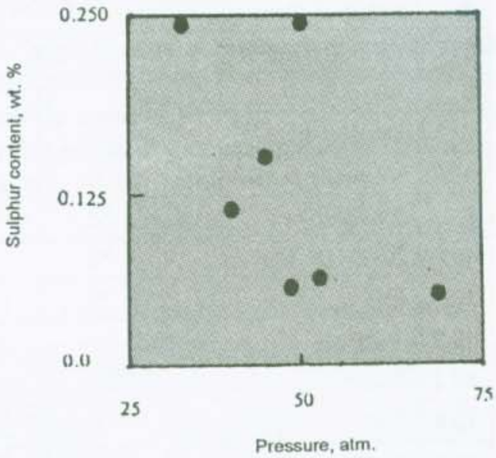


Figure 8
Influence of operating pressure of gas oil hydrodesulphurization the sulphur content of products

to meet the needs of high-speed diesel engines operating in a variety of environments throughout the world.

The changes in fuel quality such as specific gravity, volatility, ignition quality and aromatic content may be influential factors in determining smoke levels. In modern high-speed diesel engines it is difficult to detect any significant noise using fuels of 50 cetane number and above. On the other hand, there is no doubt that the use of fuels of 45 cetane number and below results in serious in combustion noise.

The ignition delay is a measure of the ignition quality of the fuels; fuels of poor ignition quality have long delay time and vice versa. For the purpose of defining, ignition quality may also be calculated from fuel inspection data. The two criteria that are most used are diesel index and calculated cetane index. Neither method is applicable to fuels containing ignition quality improver.

A large number of materials are known which have the ability to raise the cetane number of diesel fuels, such are amyl nitrate, ethyl nitrate, isopropyl nitrate and cyclohexyl nitrate. Ignition quality improvers can assist low temperature starting. Table 1 presents the current-automotive/high speed diesel oil

Table 1
Specification of Reformulated Diesel Oil and Commercial Diesel Oil in ASEAN

No.	Specifications	Units	Oct. 1993		Asia-Pacific	EC 2000	ASEAN
			CARB	US-No. 2 Diesel	2000		
1.	Sulfur Contents	wt.%	0.05	0.50	0.05	0.035	0.25-1.0
2.	Aromatic Countent	vol.%	10.0	10–20	–	–	–
3.	Polyaromatic Content	wt.%	1–4	–	–	–	–
4.	Nitrogen Content	ppm	10.0	–	–	–	–
5.	Cetane number	–	48.0	40.0	47.0	51	45–52
6.	API Gravity	–	33–34	–	Report	–	–
7.	Density at 15 °C	–	–	0.82–0.86	–	0.815	0.810–0.870
8.	Viscosity at 15 °C	cSt	2.0–4.1	1.9–4.1	2.0–5.0	–	1.5–5.0
9.	Flash Point	°C	54	52	60	–	52–66
10.	ASTM Distillation	°C					
10.1	IBP	°C	170–215	–	–	–	–
10.2	T–10	°C	205–255	–	–	–	–
10.3	T–50	°C	245–295	–	Report	–	–
10.4	T–90	°C	290–320	282–337	357	–	352–370
10.5	T–95	°C	–	–	–	350	–
10.6	Evaporated at 300°C	vol.%	–	–	–	–	40
10.7	FBP	°C	305–350	–	400	–	–

Note : CARB = California Air Resources Board
EC = European Commission

specifications, future Asia-Pacific and US diesel reformulation[3,4,5,10]. Deep hydrodesulfurization of gas oil must be done to produce diesel oil components with low sulfur and aromatic contents.

IV. REQUIREMENT IN CATALYST PERFORMANCE

A. *Hydrotreating, Process*

Hydrotreating of gas oil and automotive diesel oil blending components is currently the largest applications of this type of hydroprocessing. The primary objective in hydrotreating of these industrial oils is to enhance their quality by a reduction in aromatic and olefinic, hydrocarbons, sulfur and nitrogen impurities, and an improvement in burning caracteristics, color stability, anti resistant to sludging, using mono-functional catalyst.

If the purpose is the hydrogenation of aromatics, the hydrogen partial pressure must be higher than for hydrodesulfurization. Hydrogenation of denuclear aromatic to tetralin converts these refractory denuclear aromatics into components which crack readily to monocyclic aromatics. Naphthalene has a more pronounced olefinic character than benzene, thus its hydrogenation to the tetrahydro compounds is relatively higher compared to the benzene reaction.

If the feed containing olefins is to be hydrogenated, the partial pressure of hydrogen must also be: higher than in hydrodesulfurization, and entrance temperature to the reactor is lower so as to accelerate the hydrogenation reaction while reducing the rate of polymerization. Side reactions can occur both on the catalyst and in the exchanger and furnace preceding the reactor.

Hydrodesulfurization is always accompanied by some degree of hydrocarbon saturation resulting in loss of aromatics and olefins. Firstly, the removal of a fairly heavy molecule sulfur and its replacement by hydrogen results in a drop in specific gravity which is proportional to the amount of sulfur removal. Secondly, assuming cracking reactions are minimized, there is a lowering of the boiling-range and the formation of some light fractions.

Increasing feedstock gravity needs more severe operating conditions and the amount of low-boiling products is significant when compared with the lighter lower sulfur feedstocks.

Elimination of nitrogen by conversion into ammonia and oxygen by; conversion into water also occurs under more severe hydrodesulfurization conditions, and reduction of carbon residue and trace metallic compounds can also take place.

Temperature and pressure effects are to some extent interrelated. For example, the use of high temperature (above 430 °C) and low pressure (100 psig) promotes dehydrogenation reactions with increase laydown of carbon and thereby shortens the hours on-stream before regeneration. Combination of high pressure (1000 psig) and low temperature (315 °C) induces saturation, e.g. conversion of aromatics into naphthenes[8]. The residual sulfur content from any catalytic hydrodesulturization process is almost directly proportional to the space velocity or throughput per catalyst volume, so that doubling the space velocity doubles the residual sulfur content.

B. *Hydrotreating Catalyst*

A large variety of monofunctional catalysts can be employed for catalytic hydrotreating but the type commonly used is a mixture of metal sulfides of group VI metals promoted by sulfides of group VIII metal, supported oil alumina.

Table 1
Catalytic activity of metal sulfides couples

Type of Reactions	Order of Activity
Hydrogenation of aromatics and olefins	NiW > Ni-Mo > Co-Mo > Co-W
Hydrodesulfurization	Co-Mo > Ni-Mo > Ni-W > Co-W
Hydrodenitrogenation	Ni-Mo = Ni-W > Co-Mo > Co-W

1. The metal sites of catalyst

The metal sites of catalyst usually consist of 1 to 5% by weight of group VII metals and 5 to 20% by weight of group VIA. General observations classify the ranking of sulfides-couples of metal group VIA metal (M,S_2, and WS_2) and group VIII (Ni_3S_2 and Co_8S_9) order of activity a shown in Table 2[8].

No matter which support an metal pair of active sulfides were used, and no matter what the reaction was, the atomic ratio remains between 0.25 and 0.40 at optimum conversion.

These optima are evidence of the synergistic effect exercised by sulfides of the metals of group VIII on sulfides of the metals of group VIA[11].

Gas recycle rate has a marked effect on the carbon laydown. A high recycle rate keeps the catalyst cleaner and prolongs active life.

The influence of hydrogen content and contaminants in the make-up and recycle gases is important. In the first place, any reduction in hydrogen content by dilution with hydrocarbon gases, e.g. in make up gas from catalytic reformer which may vary from 50 to 90% by volume of hydrogen, leads to a reduction in hydrogen partial pressure which has to be compensated for by increasing the total plant pressure or reducing the space velocity.

Secondly, contaminants like carbon catalyst poisons compete for catalyst surface for conversion into methane and water vapour and also result in a lowering of hydrogen partial pressure.

As H_2S and NH_3 have low solubility in hydrocarbons they can built up an appreciable partial pressure in a unit which may suppress the activity of metal sites. The effect of hydrocarbons and other gases in reducing the hydrogen partial pressure depends a great deal on their solubility in the particular feedstock employed. By suitable adjustment of the plant pressure, it is possible to eliminate the effect and in some cases to get enrichment of hydrogen in the recycle gas streams.

2. Catalyst Support

Catalyst support of y-alumina can be used in granular, pelleted, or extrudate form. Most hydrotreated charge stocks have relatively low volatilities and thus. 0nly partially vaporized under normal hydrotreating conditions. Under such conditions, masstransfer rate may be controlling for some reactions. Slow surface reactions are less affected by diffusion than are fast surface reactions. The factors which increase turbulence and reduce the quantity of liquid presents in the reactor will increase over-all conversion by reducing diffusion resistance.

Catalyst pore diameter, pore size distribution, and particle size will influence diffusion rates to and from the catalyst surface. Thus, they are important only in processes in which resistance to difusion is the major parameter in the over-all reaction process.

The rate of diffusion through gaseous film is much greater than through corresponding liquid films. In the mixed phase reactor, hydrogen is the limiting reactant at the catalyst surface eventhough there may be a large over-all excess of hydrogen. Since the rate of hydrogen diffusion is slow through liquid hydrocarbons, catalyst sited in pores filled with liquid will be ineffective for catalyzing the hydrogen reaction.

Internal pore surfaces would be expected to be much more effective in vapor-phase reaction however. Thus in catalytic hydrogenation processes, reaction velocity increases are to be expected by decreasing catalyst particle size and by operating in such as to reduce liquid.

The factor determining minimum particles size is pressure drop, as high pressure drop increases running cost. In general the smaller the catalyst particles, the larger the pressure drop. However, particle size also affects heat and mass transfer to and from the active catalytic surface, and hence catalyst effecfiveness on catalyst particle size.

It is vital that catalyst particles have sufficient strength to resist breakage and crumbling during continuous operation as otherwise the pressure drop will increase. It is not known, especially in the past, for catalyst charges to have failed due to deterioration of strength. While high strength is associated with low porosity, other catalyst requirements, such as good mass transfer and high surface area, require the opposite.

Feed to process must be efficiently desalted and free of prticulate matters which could cause blockages in the catalyst bed[12]. One of the chief problems with the particular vanadium, on the catalyst pore, which must therefore be replaced when deactivated, and the time taken for the catalyst replacement can significantly reduce the unit time efficiently. Fixed bed catalyst tend to plug owing to solids in the feed or carbon lay-down when processing heavy feeds.

V. CONCLUSION

In ASEAN refineries, over 5,673-MBPSD of total feedstock are processed into 1.31 MBPSD gas oil products. This consists of the following product distribution: straight-run gas oil 85.44%, thermal cracked gas oil 2.52%, cat. cracked gas oil 3.50% and hydrocracked gas oil 8.54% on total gas oil products. About 50% of this total gas oil is processed in the hydrotreating processes to improve the performance of gas oil.

The quality of naphthenic straight-run gas oil, thermal and catalytic cracked gas oils must be improved by using the hydrotreating processes. In ASEAN refineries, this hydrotreating processes will play an important role in producing a high gas oil and diesel performance having sulfur content 0.05 wt.% of sulfur content and 10-20 vol.% of aromatic content. Liquid phase of gas oil hydrotreating has diffusion rate controlled, thus the performance of Al_20_3 support must be improved too, such as high porosity and low particle sizes with the high physical and mechanical properties.

Process technology currently being selected to meet reformulated diesel oil includes: to produce low sulfur diesel oil, hydrotreating to reduce sulfur and unsaturated hydrocarbons (olefins, aromatics), and two supporting units: i.e sulfur recovery and hydrogen.

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