

# ROLE OF CATALYTIC REFORMING PROCESS FOR GASOLINE PRODUCTION IN ASEAN REFINERIES

by  
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## I. INTRODUCTION

The crude oils processed in refineries range from sweet crudes, such as Southeast Asian light Crudes, to sour crude, such as Middle East, Far East, and Persian Gulf<sup>[1]</sup>.

For the period 1992-2005, the average annual demand growth rate for light products (gasoline, kerosene, diesel oil) is higher than residual fuel oil. These data clearly show that the need will continue for converting additional bottom into light products, by both thermal or catalytic conversions<sup>[2]</sup>.

The passage of the Clean Air Act Amendement 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 such as Asia-Pacific, California Air Resources Board (CARB) and European Commission (EC). Various terms in the models address qualities of the gasoline blended such as benzene, total aromatics and olefm contents, RVP, the T90 of distillation range, sulphur content, and oxygenates content<sup>[3,4,5]</sup>.

Motor gasoline is essentially a complex mixture of hydrocarbons distilling about 40°C and 220°C and consisting of compounds generally in the range C<sub>5</sub> to C<sub>12</sub>. Gasoline components can be produced by both the distillation of crude oil and the conversion of the crude oil fraction.

Catalytic reforming process using bifunctional catalyst converts low octane number heavy naphthas into reformat with a high octane number. Bifunctional catalyst containing metal site (Pt, Pt/Ge) and acid site (Al<sub>2</sub>O<sub>3</sub>Cl) are generally used. The balance is most important in a bifunctional reforming catalyst, and in fact it has to be different for different duties<sup>[6]</sup>.

The end point of the naphtha feedstock is usually limited to about 185°C, partially because of increased

coke deposition on the catalyst. The reforming catalyst exhibits a sensitivity to the conventional impurities of naphtha feed, such as: water (moisture), organic compounds of chlor, nitrogen and sulphur, and organo-metallic compounds (lead, copper, iron). Sintering of the metal phase becomes effective only beyond 500°C as measured by lowering of the dispersion of platinum atom condition, at the same time coke formation on the catalyst increases too<sup>[6,7]</sup>.

The life of the catalyst will depend both on its stability and regenerability, expressed either in months or year, or in tonnage treated for unit weight of catalyst. This paper presents briefly composition of gasoline pool, specification of commercial gasoline in Indonesia as well as ASEAN refineries, the catalyst improvements, catalyst deactivation and catalyst regeneration of the reforming process.

## II. CATALYTIC REFORMING PROCESS IN ASEAN REFINERIES

Gasoline blending components are essentially complex mixtures of hydrocarbons distilling between about 40° and 220°C, consisting of compounds generally in the range of C<sub>5</sub> to C<sub>12</sub>. These gasoline components can be produced from both the distillation of crude oil and hydroconversion of the crude oil fractions i.e. by cracking, reforming, isomerization, alkylation and polymerization processes. Small amounts of additives are also used to enhance various aspects of the performance of the fuel<sup>[6,8]</sup>.

From its hydrocarbon composition point of view, gasoline components can be classified as follows: paraffmic gasoline components (atkylate, isomerase, light straight-run naphtha and light hydrocracked naphtha), olefinic gasoline components (polymer gasoline, catalytic cracked gasoline, thermal reformat) and aromatic gasoline components (reformat)<sup>[8]</sup>.

The octane levels of gasoline components produced from various refinery processes can be classified as follows: low octane gasoline components having clear RON between 45 to 65 (heavy straight-run naphtha and heavy hydrocracked naphtha), medium octane gasoline components having clear RON from 73 to 83 (light straight-run naphtha, light hydrocracked naphtha and isomerate) and high octane number of gasoline components with clear RON from 87 to 107 (thermal reformat, reformat, catalytic cracked gasoline, alkylate and polymer gasoline)<sup>[8]</sup>.

Different hydrocarbons show marked variations in their pre-flame and ignition characteristics and so differ in their combustion behaviour and knocking tendency in an engine. A motor gasoline which is satisfactory at low engine speeds must have high RON and performs well as the speed increases would have a high motor octane number (MON); in other words, a good gasoline would have a low sensitivity (S) where  $S = \text{RON} - \text{MON}$ . The sensitivity of gasoline component increases with its olefin and aromatic contents; thus those thermal cracked gasoline, thermal reformat, polymer gasoline, catalytic cracked gasoline and

reformat give high sensitivity.

Reformat has low-octane paraffin components in the lower boiling end and may comprise quite high-octane aromatic components at higher boiling end, reformat gives bad octane distribution<sup>[6]</sup>.  $C_5$  and  $C_6$  iso paraffins of light isomerized gasoline can provide excellent high octane components in the lower boiling end. They are useful to supplement those lower boiling end reformates to produce a high octane blended gasoline with a good octane distribution. Octane distribution of reformat is presented in Table 1<sup>[9]</sup>. Cat. cracked gasoline and alkylate give a good octane distribution.

In ASEAN refineries, catalytic process for production of gasoline components are as follows: catalytic cracking, reforming, isomerization, akylation and polymerization. The first two catalytic processes contribute the highest production of gasoline components i.e: about 25 and 65% vol. of the total gasoline components for cat. cracked gasoline and reformat, respectively. Production of reformates for gasoline components is quite high i.e: from 47% vol. (Indonesia) to 100% vol. (Brunei Darussalam) compared to

Table 1  
Octane distribution and hydrocarbon composition of reformat

Boiling range °C	Vol. %	Hydrocarbon composition, vol. %			Clear RON
		Paraffin	Naphtha	Aromatic	
25-45	13.6	100	0	0	82
45-63	7.6	98	2	0	80
63-75	6.9	86	5	9	62
75-85	6.9	60	5	35	81
85-95	6.3	89	7	4	64
95-107	3.9	71	9	20	70
107-120	15.3	19	3	78	96
120-130	0.8	43	0	57	88
130-140	12.3	7	0	93	104
140-150	5.6	2	0	98	115
150-170	11.8	0	0	100	111
170-185	9	0	0	100	113
25-185	100	43	2	55	96

37% vol. for reformed gasoline<sup>[10,11]</sup>. Isomerate and alkylate productions have little contributions: i.e about 5% vol. and <1 % vol. of the total gasoline components respectively<sup>[10]</sup>.

Exhaust emission in gasoline engines can be reduced by decreasing the RVP, T50, T90, distillation range, and sulfur, olefin, benzene and total aromatic content of gasoline. ASEAN gasoline pool leans to much to reformat with high benzene and aromatic contents, T90 distillation and lack in alkylate and isomerate having low sensitivity and good octane distribution.

Specification of reformulated gasoline proposed in the USA and European are much stricter than those for commercial gasoline in ASEAN<sup>[3,4,5,10,12]</sup>. Production of reformulated gasoline in ASEAN can be realized by increasing the capacity and performance of prefractionation, fractionation of reformat and cat. cracked gasoline, and FCC units in the existing refineries.

Prefractionation and splitting of naphtha reformer feeds can reduce reformat benzene content to less than 1 % vol. from about 5% vol. The existing naphtha hydrotreater can be used to saturate the olefin of cat. cracked gasoline.

Catalytic reforming converts a low octane number of naphtha (i.e. heavy straight run naphtha, heavy thermal cracked naphtha and heavy hydrocracked naphtha) into reformat with high octane number using bifunctional reforming catalyst (monometallic and bimetallic reforming catalyst).

There are currently 33 units of catalytic processes in ASEAN countries with the total capacity about 451 MBPSD using both monometallic and bimetallic bifunctional catalyst with two types of process technology (semiregenerative.-SEMI and continuous catalyst regeneration-CCR) i.e. Brunei Darussalam 1 SEMI; Indonesia 3 SEMI and 4CCR; Malaysia 5 SEMI and 2 CCR; Philippines 4 SEMI; Singapore 3 SEMI and 5 CCR; and Thailand 2 SEMI and 6 CCR<sup>[10]</sup>

Production of reformat with a high yield and high octane number from low quality feedstocks (high paraffin content and high impurity) needs a severe

operating condition (low operating pressure, low hydrogen hydrocarbon ratio, and high operating temperature) with a high catalyst performance. High operating pressure and high paraffin content of naphtha feedstock decrease yield and research octane number (RON) of reformat. RON of reformat depends on the feedstock composition, yield of reformat and catalyst (Table 2)<sup>[9]</sup>, and increases with the aromatic content of reformat.

Reformats have the following performances: high RON (87-107), low RVP (35-58 kPa); high Driveability Index (580-690°C); high total aromatics (45-70 vol.%); high benzene (3-8 vol.%) and high sensitivity (8-14) (Table 3)<sup>[6,9,10]</sup>.

### III. DEVELOPMENT IN REFORMING CATALYST

#### A. Bifunctional Reforming Catalyst

Reforming catalyst is a bifunctional catalyst containing metal site (platinum) and acid site (halogenated alumina). Platinum content of the catalyst is normally in the range 0.3-0.8 per cent wt. Normally, the high-platinum catalyst (0.6-0.8 per cent wt.) are used for severe operations such as the production of 100 octane number gasoline from feed with high paraffin content<sup>[6]</sup>. At higher Pt content there is some tendency to effect demethylation and naphthene ring opening by hydrogenolysis reaction, which is undesirable, while at lower levels the catalyst tends to be less resistant to poisons. Hexane distribution of methyl cyclopentane hydrodeacyclization products by

**Table 2**  
Influence of (N+2A) naphtha feed on the yield and clear RON of reformat

Naphtha feeds (N+2A), vol. %	Reformat, Clear RON			
	100	95	90	85
	Yield, vol. %			
40	63	72	77	82
50	68	76	81	85
60	73	79	85	89
70	77	84	88	92

Note: N = Naphthene and A = Aromatic

Table 3  
Performance of reformates

Characteristic	Units	Reformate		Reformate		Reformate		Reformate		Reformate		Reformate		Reformate	
		Feed	Reformate	Feed	Reformate	Feed	Reformate	Feed	Reformate	Feed	Reformate	Feed	Reformate	Feed	Reformate
Yield	vol. %	-	69	-	80	-	79,8	-	80	-	80	-	80	-	78
Distillation	°C														
- IBP		90	35	90	46	98	49	80	48	98	48	80	48	35	
- 10 vol %		110	60	105	80	119	92	100	76	119	76	100	76	79	
- 30 vol %		115	93	115	105	-	110	107	-	-	-	107	-	109	
- 50 vol %		125	115	120	130	133	120	115	126	133	126	115	126	135	
- 70 vol %		135	135	135	150	-	133	125	-	-	-	125	-	-	
- 90 vol %		145	158	150	170	152	155	140	161	152	161	140	161	159	
- FBP		175	186	175	205	157	187	180	197	157	197	180	197	202	
Driveability Index (D1)	°C	-	593	-	680	-	653	-	653	-	653	-	653	-	682,5
Clear RON	-	-	95,2	-	101	-	102,5	-	98	-	98	-	98	-	93,5
RVP	kPa	-	52	-	-	-	-	-	-	-	-	-	-	-	-
Hydrocarbon Composition	vol. %														
- Naphene		29	-	23	1	17,9	0,75	47,5	2,2	17,9	2,2	47,5	2,2	0	
- Aromatic		9	60	12	71	12,4	8,25	8,5	64,7	12,4	64,7	8,5	64,7	54,5	
- Paraffin		62	40	65	2,8	69,3	18	43,5	33,1	69,3	33,1	43,5	33,1	45,5	
- Benzena*		-	-	-	3,2	-	3,5	-	-	-	-	-	-	-	

Note: \* = wt.%, N = Naphtha, A = Aromatic and P = Paraffin

hydrogenolysis and hydrocracking mechanisms is presented in Table 4<sup>[13,14]</sup>. The acid activity can be obtained by means of halogens (usually fluorine or chlorine) up to about 1 per cent wt. in catalysts. The purpose of platinum on the catalyst is to promote dehydrogenation and hydrogenation reactions, i.e. the production of aromatics, participation in hydrocracking and rapid hydrogenation of carbon forming precursors.

Carbon can cover and fully poison flat surfaces easier than edges and corners of the Pt-crystallite. In the case of the small particle size of monometallic reforming catalyst, reactant spent less time in the platinum zones, thus low carbon deposition is produced.

The latest development is the use of bimetallic reforming catalyst which incorporates other metals (rhenium, germanium, tin) in addition to platinum. The second metal can modify the aluminium support so as to maximize the platinum surface area (or low particle size), produce an alloy with platinum having high melting point (low sintering) and also this alloy would destroy coke precursor that formed in the platinum zones. Thus this bi-metallic catalyst can be operated at lower hydrogen partial pressure than can the monometallic platinum catalyst without deactivation. It is thus possible to take advantage of the increase in yield and aromatic control of gasoline associated with lower pressure operation without incurring the penalty of short catalysts life<sup>[6,15]</sup>. Yield, octane number and hydrocarbon composition of reformat with mono and bimetallic reforming catalysts is given in Table 5<sup>[16]</sup>.

### B. Deactivation of Catalyst

Feedstock end point is usually limited to about 185°C partially because of increased coke deposition on the catalyst as the end point increases. The length of time between regenerations will be reduced about 20-30% by changing a 430°F. e.p. compared to a 400°F. e.p. virgin naphtha<sup>[6,8]</sup>.

Organic chloride compounds in the feedstock promote or overpromotes hydrocracking function of

**Table 4**  
Composition of methylcyclopentane hydrodeacyclization products using mono and bi-metallic reforming catalysts

Composition of Products		Reforming catalyst	
		Mono-metallic	Bi-metallic
1. N.Hexane	mol %	39.18	91.74
2. Methyl pentane	mol %	42.8	3.61
3. Methyl pentane	mol %	18.02	4.65

**Table 5**  
Performance of reformat using mono and bi-metallic catalyst

Reformat		Reforming catalyst	
		Mono-metallic	Bi-metallic
Yield	voL%	70.93	75.23
Hydrocarbon compositions	voL%		
- Paraffin		32.6	2L5
- Naphthene		10.5	9.2
- Aromatics		56.9	69.3
- Clear RON		95.2	98.4

the catalyst i.e. increasing hydrocracking of paraffins, C<sub>5</sub>-ring splitting and hydroisomerization, but this hydrocracking function will decrease by injection of water<sup>[6]</sup>. If there is as much as 2 ppm halides in the feedstock, it is adding to acid function of the catalyst. It takes 50 ppm of water to keep this in balance<sup>[6]</sup>.

Organic nitrogen compounds are converted into ammonia under reforming condition, and this neutralizes acid sites on the catalyst and thus represses the activity for isomerization, hydrocracking and dehydrocyc lization reactions<sup>[8,17]</sup>.

The effect is generally felt to be reversible and by removing the nitrogen from the feed, it regains the activity level of catalyst. Thus it pays a penalty for nitrogen no matter how little its content, both in reduced octane and in fouling problem as well. No problem for regenerative process with <0.5 ppm of nitrogen; but when it gets up to 1.5-2.0, it costs more temperature for the same octane number.

The metal function is inhibited by sulfur compound, which are transformed into hydrogen sulfide on the catalyst. Sulfur actually acts as platinum sulfidation agent. At operating temperatures and hydrogen partial pressures equilibrium is established<sup>[6,7,8,17]</sup>. The optimum content for the sulfur in the charging stock is lower than 1 ppm and 1 ppb sulfur for mono and bimetallic reforming catalyst, respectively. It certainly makes for longer cat life and neater operation.

Also, the presence of some foreign metals is known to modify the hydrogenating-dehydrogenating activity of the catalyst. Lead or arsenic, among others, form stable associations with platinum that cause an irreversible deactivation of catalyst. Other metals, such as copper or iron, also modify the catalytic behaviour i.e. change the dehydrocyclization activity 460 ppm by weight copper and 0.5% of iron<sup>[6,8,15,17]</sup>.

Sintering of the metal phase becomes effective only beyond 500°C as measured by lowering of the dispersion of platinum atom condition, at the same time coke formation on the catalyst increases too<sup>[6]</sup>.

### C. Regeneration of Catalyst

The regenerability of the catalysts is characterized both by the number of regenerations it can undergo and by the extent to which it stands successive regenerations. The life of the catalyst will depend both on its stability and regenerability, expressed either in months on years or in tonnage treated for unit weight of catalyst<sup>[6]</sup>.

Coke is eliminated by burning in air or oxygen diluted with nitrogen, while taking the necessary precautions to avoid an excessively high temperature. The maximum temperature is around 550°C, beyond which the supports loose surface and mechanical resistance<sup>[6]</sup>.

Water in the recirculating flue gas, formed from burning hydrogen in the catalyst coke, can also cause hydrolysis of the halides on the catalyst and in turn causes corrosion in the plant. Thus after coke combustion the catalyst generally contains 0.6-0.8wt.% chlorine compared to 0.9-1.3 for new catalysts<sup>[6]</sup>.

The catalyst must be reloaded with chlorine compounds such as free chlorine, hydrochloric acid or organic derivatives like carbon tetrachloride or dichloropropane. It adds 5 ppm of chloride almost immediately on starting the feed back into the unit.

After rechlorination comes a final calcination, which has proven important for redispersing the metal. The mechanism of the attack on the platinum crystallites in oxidizing atmospheres is not very well known, but the suggested hypotheses call for formation of volatile complexes of platinum. By keeping the optimum chlorine content in the reforming catalyst, the catalyst stability and the platinum dispersion during catalyst regeneration can be increased.

The method of regeneration can have a drastic effect on catalyst life. It is possible to regenerate catalyst with little permanent loss in performance.

### IV. CONCLUSION

ASEAN gasoline pools lean too much to reformate for reduction of exhaust emission in gasoline engines and lack in alkylate and isomerate having low sensitivity and good octane distribution.

Reformates have high clear RON (87-107), high sensitivity and bad octane distribution. Reduction of benzene content of reformat can be realized by both prefractionation of naphtha feedstock and the fractionation of reformat.

Reforming catalyst is a bifunctional catalyst containing metal site (platinum) and acid site ( $Al_2O_3-Cl$ ). The balance of those two types of metal sites most important in a reforming catalyst. Latest development of this reforming bifunctional catalyst involves the use of bimetallic reforming catalyst which incorporates other metals (rhenium, gallium, tin).

The reforming catalyst exhibits a sensitivity to the impurities of naphtha feed, such as water (moisture), organic compounds of chlor, nitrogen and sulphur, and organo-metallic compounds. Sintering of the metal phase becomes effective only beyond 500°C as measured by lowering of the dispersion of platinum. The life catalyst depends both on its stability and regenerability.

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