CHAPTER II
LITERATURE SURVEY

2.1 Types of Aromatic Compounds in Petroleum Fractions

The aromatic compounds in petroleum are classified into four types: (i) monoaromatics, (ii) diaromatics, (iii) triaromatics, and (iv) polycyclic aromatics (Stanislaus and Cooper, 1994). Among such compounds, the polycyclic aromatics type with four or more condensed benzene rings, is largely presented in a high-boiling petroleum fraction (BP > 350°C) whereas the other three are important components of middle distillates. In unhydrotreated oil or straight-run gas oil, the diaromatics (mainly alkyl naphthalenes) constitute a major portion in the mixture. However, in hydrotreated oil, monoaromatic compounds are present in large quantities. Since the hydrogenation of the last aromatics ring is more difficult than that of condensed multi-ring aromatics (Stanislaus and Cooper, 1994) the hydrogenation of the monoaromatics is a key step in the production of low-aromatic diesel fuel.

2.2 Revolution of the Refining Process

According to general fuel regulations, the refining process has started to produce low sulphur and aromatic contents in a wide range of crude oil using metal sulphide on an alumina support. At the beginning, desulphurization became a major issue whereas dearomatization was only of minor importance. Sulfur compounds are converted to SO_x during combustion, which not only contribute to acid rain, but also poison the catalytic converter for exhaust emission treatment. Then the removal of aromatics in distillate feedstock was focused on more since it was found that the reduction of aromatics was related to the lowering of particulate matter, NOx emission (health risk) and the improvement of combustion efficiency (Rautanen *et al.*, 2001). However, the activity of such catalysts at normal diesel hydrotreating pressure was insufficient to obtain a high degree of aromatic saturations. In order to meet the stringent regulations, high temperatures, high hydrogen pressures and low space velocities are required (Cooper and Donnis, 1996). Since, these severe operating conditions have lead to thermodynamic equilibrium limitations in aromatic conversions and economically unfeasible solutions as well. Recently, the two-stage process (shown in Figure 2.1) using catalysts with high desulphurization activity (NiMo, CoMo, and NiW on Al_2O_3) in the first stage and metal catalysts with high hydrogenation activity (e.g. Pt, Pd, and Ni on Al_2O_3) in the second stage is known as a high efficiency conventional process to decreased sulphur and aromatic concentration. Several two-stage processed have been proposed by Shell, IFP, Amaco, PopsØe, Criterion/ Lummus, Akzo and UOP.

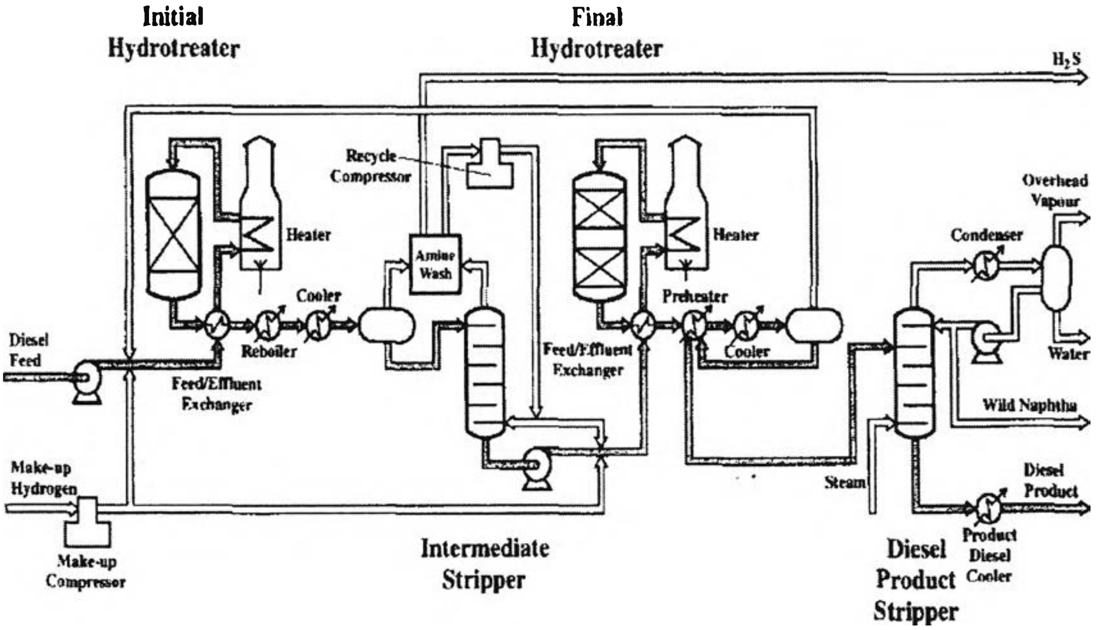


Figure 2.1 Diagram of a two-stage process for diesel aromatics removal (Søgaard-Andersen et al., 1992).

2.3 Future Aspects

Aromatic compounds constitute a large fraction of premium gasoline due to their high resistance to knock. However, aromatic concentrations in European gasoline have been limited since the year 2000 to 42% by volume, and is planned to be 35% in the near future. In diesel fuel, the aromatic content is lower than that in gasoline. Recently, the limitation of poly-aromatics content is anticipated to be 11% by mass in European diesel fuel.

In the near future, the more extensive removal of aromatic compounds will be a concern for both diesel and gasoline fuels. In addition, a significant increase in cetane number, which is one of the very important properties of diesel fuel has, been required (Cooper and Donnis, 1996). Typically, an increase in cetane number can be achieved by several methods. The first option is the addition of cetane boosters (e.g. alkyl nitrates). Their action occurs at the elementary step of oxidation before the ignition. As a result, ignition delay, combustion noise and particulate matters are reduced (Lee *et al.*, 1993; Nandi *et al.* 1994; Nandi, 1996; and Suppes *et al.*, 1999). In addition, cold-start performance is also improved. However, the cetane boosters may be hazardous and degrade the storage stability of the fuel. The second alternative is a blend with Fischer-Tropsch (FT) gas-to-liquid diesel fuel. It also results in the reduction of the concentration of aromatic compounds, sulfur and other impurities. This option, however, may not be an economically viable solution when FT is extensively blended. Another alternative is deep hydrogenation. This process, the increase in cetane number is strongly depended on the nature of crude and refinery blending strategies. Nowadays, diesel oil is a blend of cuts coming from primary distillation, hydrocracking units, FCC light cycle oil, and also some products obtained by thermal treatments such as visbreaking or coking. Recently, more light cycle oil (LCO) was added in the diesel pool. Due to its high contents of aromatics and low cetane numbers (typically between 20 and 30), the incorporation of LCO has a negative impact on cetane number. Although most of the aromatics in LCO are saturated in deep hydrogenation, the cetane number is still lower than the specifications.

In the past few years, it has been proposed that an increase in cetane number to approach the requirements in the future could be achieved by coupling the hydrogenation of aromatics with the ring opening reaction (Snamprogetti and Milanese, 2003).

2.4 Hydrogenation of Aromatics

The hydrogenation of aromatics is considered to be a reversible reaction (Stanislaus and Cooper, 1994). Typically, heterogeneous catalysts are employed, especially for large-scale production. The hydrogenation typically takes place on noble and other group VIII metal catalysts. However, it is difficult to reach complete conversion due to equilibrium limitations. The hydrogenation of an aromatic species, A, is given by:

$$A + nH_2 \leftrightarrow AH \qquad (2.1)$$

where AH is the hydrogenation product. Thus the equilibrium concentration can be approximated by:

$$\frac{Y_A}{Y_A + Y_{AH}} = \frac{1}{1 + K_a \times (P_{H_2})^n} \qquad (2.2)$$

where Y_A is the equilibrium concentration of aromatics;

Y_{HA} is the equilibrium concentration of hydrogenation product;

K_a is the equilibrium constant; and

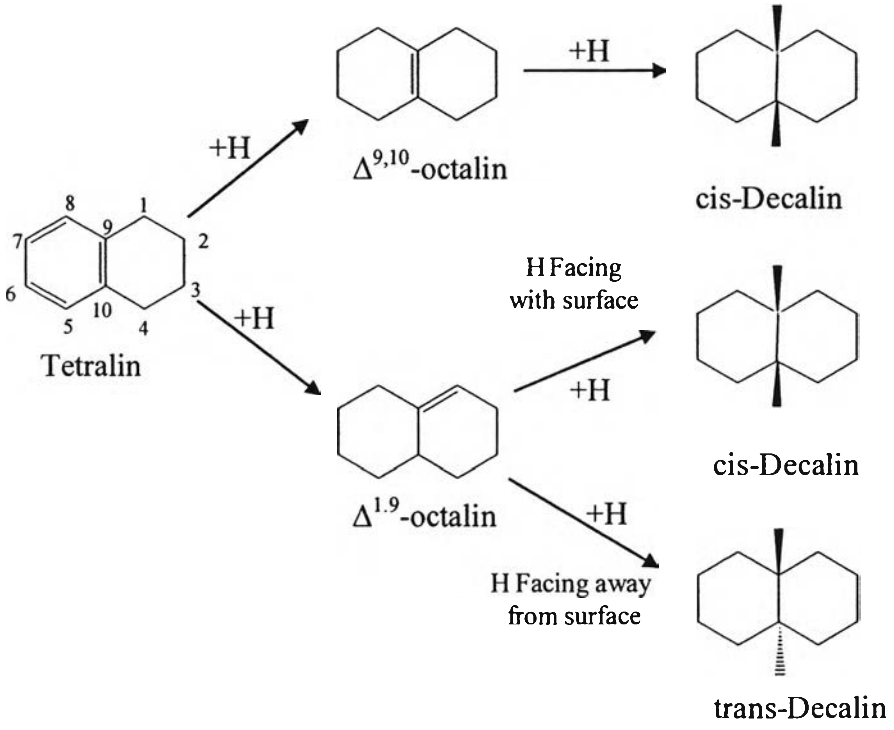
P_{H_2} is the partial pressure of hydrogen.

The hydrogenation of aromatics is highly exothermic with the heat of reaction typically in the range of 63-71 kJ/mole H_2. The rate of the surface reaction is depended on reaction temperature since adsorption and desorption processes on the surface, and of external and internal diffusions (Ertl et al., 1997).

The adsorption and hydrogenation of aromatic hydrocarbons on group VIII metals have been extensively studied. It was proposed that the hydrogenation of aromatics on these metals involved a π-complex adsorption mechanism (Stanislaus and Cooper, 1994). The metal influenced both the characteristic adsorption/ desorption and the surface reaction. Metals possessed inherent selectivity profiles which arise from the different adsorption/desorption enthalpies of the adsorbates on the various metals, and their activation energies for the surface reaction.

The different reactivities for subsequent ring-contraction and ring-opening reactions of two isomers, cis- and trans-decalin, over HY catalysts were observed (Santikunaporn *et al.*, 2004). It was found that cis-decalin preferred to produce C_{10} products (ring-contraction or ring-opening products). In contrast, trans-decalin, which is the more stable isomer of the two, was difficult to react, but when it did, cracking products were mainly obtained. Therefore, cis-decalin would be an important isomer to facilitate ring opening products in the subsequent process.

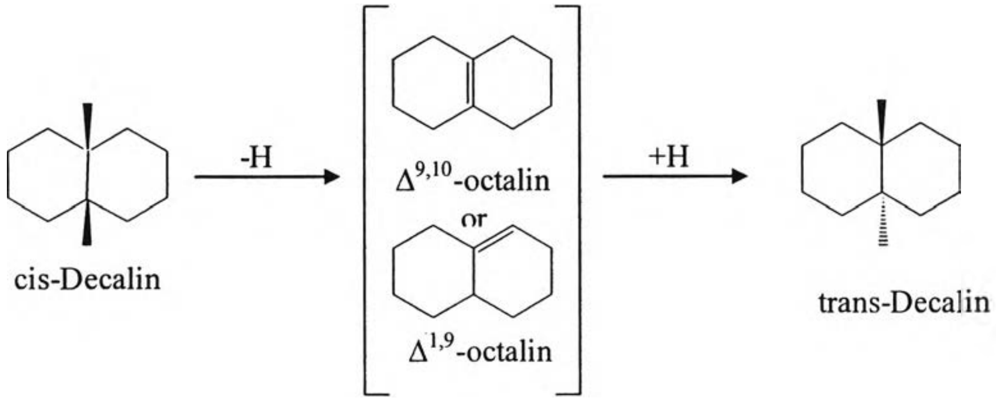
The tetralin hydrogenation pathway was investigated by Weitkamp and co-workers (1968). They proposed that tetralin was firstly hydrogenated via $\Delta^{9,10}$-octalin or $\Delta^{1,9}$-octalin intermediates. Then, these intermediates were further hydrogenated to cis- and trans-decalin products as shown in Scheme 2.1. In addition, cis- to trans-decalin isomerization was also observed. The formations of cis- and trans-decalin were explained in terms of gas phase intermediates. The hydrogenation of $\Delta^{9,10}$-octalin intermediate which has the double bond in the bridging position would yield only cis-decalin since the addition of the two hydrogen atoms occurs from the same side. In contrast, the hydrogenation of $\Delta^{1,9}$-octalin intermediate provided cis- and trans-decalin which was explained in terms of its orientation. However, the formation of cis- and trans-decalin products was mostly dependent on $\Delta^{1,9}$-octalin intermediate since the hydrogenation rate of this intermediate is apparently much higher than that of $\Delta^{9,10}$-octalin. Once the hydrogen atom in position 10 of $\Delta^{1,9}$-octalin is adsorbed facing towards the surface and the addition of the two hydrogen atoms to positions 1 and 9 occurs on the same side, the cis-decalin isomer is produced. On the other hand, if the hydrogen atom in position 10 faces away from the surface and the hydrogen incorporation occurs on the opposite side, trans-decalin is consequently obtained. Alternatively, desorption of the $\Delta^{1,9}$-octalin may not be necessary for the formation of trans-decalin since it may roll over on the surface and get hydrogenated on the opposite site.



Scheme 2.1 Reaction pathways of tetralin hydrogenation (Weitkamp *et al.*, 1968).

In previous work, the hydrogenation of tetralin on Pt/Al_2O_3 and Pd/Al_2O_3 catalysts was studied (Jongpatiwut *et al.*, 2004). It was shown that the trans/cis-decalin ratio depended on the tetralin conversion and the catalyst used. At low tetralin conversion, the intrinsic properties of each catalyst were revealed. The observed trans/cis-decalin ratio on Pd was around 3 times higher than that on the Pt catalyst. At high tetralin conversion, the trans/cis-decalin ratio was continuously increased due to the cis- to trans-decalin isomerization.

Typically, stereoisomerization is known as a reversible reaction. However, the isomerization from trans- to cis-decalin is not taken into account because the forward reaction of cis- to trans-decalin is much faster than the backward reaction (Lai and Song, 1996). Hence, the cis- to trans-decalin isomerization could be treated as an irreversible reaction (Huang and Kang, 1995). The isomerization was proposed through a two-step process as shown in Scheme 2.2. The cis-decalin was firstly dehydrogenated to olefinic intermediates, and then further hydrogenated to the trans-decalin isomer. It was observed that both the dehydrogenation and hydrogenation reactions take place on metal catalysts. Therefore, in order to maximize the cis-decalin products to facilitate ring opening products in the subsequent process, the intrinsic properties of the catalyst selected should prefer to produce cis-decalin and to minimize cis- to trans-decalin isomerization at the same time.

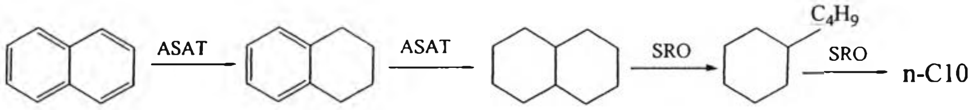


Scheme 2.2 Reaction pathway for isomerization of cis- to trans-decalin (Huang and Kang, 1995).

2.5 Ring Opening Reactions

2.5.1 Ring Opening of Naphthenic Molecules

The ring opening of naphthenic rings is one of the promising reactions for boosting cetane number which has been projected for the future legislation (Cooper and Donnis, 1996; Arribas and Martínez, 2002). A simplified scheme for the proposed aromatics saturation (ASAT) plus selective ring opening (SRO) naphthenic upgrading chemistries is shown in Scheme 2.3. The saturation of naphthalene to decalin, requiring the addition of 5 moles of hydrogen, improves both density and cetane number. Even though the lowest density achievable by the complete saturation of naphthalene is close to 0.9 and the maximum cetane number is about 38, in order to comply with the anticipated diesel specifications of a density less than 0.85 and a cetane number greater than 40, the substantial product improvements are necessary.



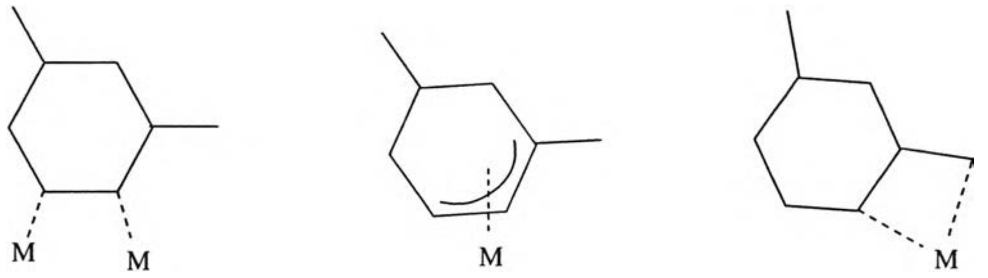
Density (g/cm^3)	1.025	0.973	0.896	0.799	0.730
Blending cetane number	10-20	15-20	35-38	58-62	72.76
	Naphthalene	Tetralin	Decalin	Butyl-cyclohexane	Decane

Scheme 2.3 Aromatics saturation (ASAT) of multiring aromatic followed by selective ring opening (SRO) provides density and cetane number benefits (McVicker *et al.*, 2002).

In order to achieve the ring opening, the aromatic is firstly hydrogenated to a naphthenic ring which is further reacted to obtain the ring opening products. In recent work, the ring opening of alkylsubstituted cyclopentanes and bicyclonaphthenes on Ir/Al_2O_3 catalyst was studied (McVicker *et al.*, 2002). The ring opening of alkylcyclohexanes on Ir catalysts was one to two orders of magnitude lower than that of alkylcyclopentanes. It was recommended that the introduction of an acidic function in the catalyst was required in order to catalyze the C_6 to C_5 contraction thus facilitation ring opening of the alkylcyclopentanes on the Ir sites (Vasina *et al.*, 2001). Therefore, the presence of a Brønsted acid site may be essential for the accomplishment of both isomerization and ring opening. In addition, the catalyst activity increases with increasing reaction temperature.

The opening of the naphthenic rings can occur on either acidic or metallic catalysts. On an acidic catalyst, the C–C bond in the beta position from the tertiary carbon is favored to break. Therefore, the corresponding products are branched chain hydrocarbons which makes acid catalysts as a potential candidate for octane improvement (Arribas and Martínez, 2002; and Kubička *et al.*, 2004). However, the drawbacks of acid catalysts are the excessive cracking to lower molecular weights and fast deactivation due to coke formation.

The ring opening of naphthenic compounds over metal catalysts takes place via different mechanisms such as: dicarbene, π-adsorbed olefin or metallocyclobutane (Gault *et. al.*, 1981; Foger 1982; and Foger and Jaeger, 1989). The three different modes of ring opening on metal catalysts are illustrated in Figure 2.2. The dicarbene reaction path is associated with the rupture of unsubstituted C-C (C2-C2) bonds to produce branched molecules. This mechanism may be required for octane number improvement. In contrast, in the other two mechanisms, substituted C-C bonds (e.g. C3-C2, C3-C3) are preferentially broken, which resulted in alkane products with high linearity. An improvement in cetane number may be achieved via these two mechanisms. Although the catalyst allows any of the reaction paths to operate, the reaction path with the lowest activation energy will occur. It was found that the activation energy for π-adsorbed olefin is significantly higher than that of the dicarbene mode; for example, an activation energy of 240 kJ/mol for hydrogenolysis of neopentane, in which the dicarbene mode is not possible, and a much lower activation energy of 170 kJ/mol for n-butane hydrogenolysis, a typical dicarbene reaction (Foger and Jaeger, 1989; and Foger 1982). Alternatively, the cleavage of the C-C bond via a metallocylobutane intermediate consisting of a metal atom and three C atoms, that would allow the opening of substituted C-C bonds if an external methyl group were involved in the intermediate, was proposed (Gault *et. al.*, 1981). However, the activation energy of the reaction path via the metallocyclobutane mechanism is higher than that via dicarbene mechanism. Thus this path could be operative only when the lower-evergy dicarbene path was blocked. Recently, it was proposed that the metallocyclobutane mechanism is operative in the hydrogenolysis of 2,2,3,3-tetramethylbutane on Ru catalysts since the structure of this molecule is particularly suited for the formation of metallocyclos rather than dicarbenes (Coq *et al.*, 1995).



(I) dicarbene mode (II) π-adsorbed olefin mode (III) metallocyclobutane mode

Figure 2.2 Ring opening mechanisms on metal catalyst (Do *et al.*, 2006).

Selective ring opening can be carried out on certain noble metals such as Pt, Pd, Ir and Rh supported on alumina or silica. These catalysts are generally known as effective catalysts for the ring opening of methylcyclopentane to C6 alkanes (Gault, 1981). The effect of metal particle size of Pt/Al_2O_3 catalysts was also studied. The breakage of any endocyclic C–C bonds followed the statistical number on highly dispersed Pt on Al_2O_3. In contrast, secondary–secondary C–C bonds (C2-C2) were preferentially broken on a large Pt cluster (Gault, 1981).

The outstanding hydrogenolysis activity of Ir compared to other group VIII transition metals is found in literature (Plunkett and Clark, 1974; Karpinski and Clarke, 1975; Sinfelt, 1969; and Boudart and Ptak, 1970). The ring opening of 1,3-dimethylcyclohexane (1,3-DMCH) on TiO_2, Al_2O_3 and SiO_2 supported Ir catalysts was also investigated (Do *et al.*, 2006). The primary products from the ring opening of 1,3-DMCH are classified into two groups. The breakage of tertiary-secondary C-C bonds (a and b in Figure 2.2) yields 2-methylheptane (2-MC7) and 4-methylheptane (4-MC7) products, while 2,4-dimethylhexane (2,4-DMC6) is formed by the cleavage of a secondary-secondary C-C bond (c in Figure 2.2). The (2-MC7 + 4-MC7)/2,4-DMC6 ratios which represent a catalyst with high-cetane selectivity on Ir/TiO_2, Ir/Al_2O_3 and Ir/SiO_2 catalysts are illustrated in Figure 2.2. A dramatic difference in the ratios was found when the support was varied. It was proposed that the preferred pathway of ring opening of 1,3-DMCH on TiO_2, Al_2O_3 and SiO_2 supported Ir catalysts appears to be related to a support effect rather than to an effect of metal dispersion. Thus silica-support catalysts with low metal dispersion would be useful in gasoline production. In contrast, the metallocylcobutane mode becomes operative leading to the more desirable opening of tertiary-secondary C-C bonds (substituted positions) for products of high cetane number on Ir/TiO_2, and Ir/Al_2O_3 catalysts.

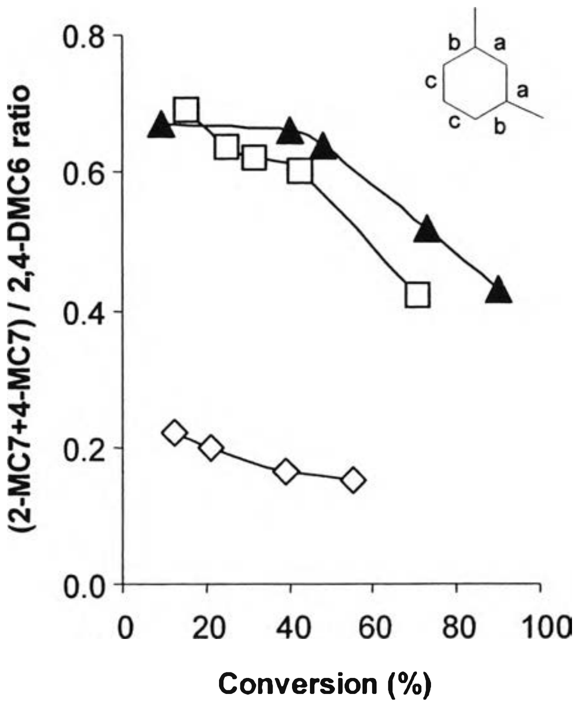


Figure 2.3 Ratio of substituted C-C cleavage to unsubstituted C-C cleavage of 1,3-DMCH over Ir on different supports. Without considering secondary hydrogenolysis, the ratio of (2-MC7 + 4-MC7)/2,4-DMC6 would represent the ratio of (a+b)/c cleavage (the statistical value of (a+b)/c is 2). ▲= Ir/Al_2O_3; ◊ = Ir/SiO_2; □ = Ir/TiO_2 (Do *et al.*, 2006).

2.5.2 Cetane Number of the Ring Opening Products

In a previous work, the possible ring opening reaction pathways and the estimated cetane number of each individual compound were proposed (Santana *et al.*, 2006). The cetane number (CN) of each hydrocarbon was calculated using an artificial neural network program that was trained with the pure compound cetane number from a database. The great challenge to reach high cetane number products was mentioned. For example, it was proposed that using acidic catalysts alone was not able to obtain products with a cetane number significantly higher than decalin feed, as illustrated in Figure 2.4, and Tables 2.1-2.3. It was shown that no significant gain in CN could be expected from the ring opening products even though the ring opening took place on metal catalysts via dicarbene mechanism as shown in Figure 2.5. To yield higher cetane number products, it is necessary for the ring to break only at the subsitituted C-C bond position, as shown in Figure 2.6. In the case of the ring opening of perhydrophenanthrene, a significant increase in cetane number is impossible (Figure 2.7). In addition, extensive hydrogen consumption is required to upgrade the cetane number. The minimized branching using the selective ring opening reaction is necessary to obtain high cetane number products.

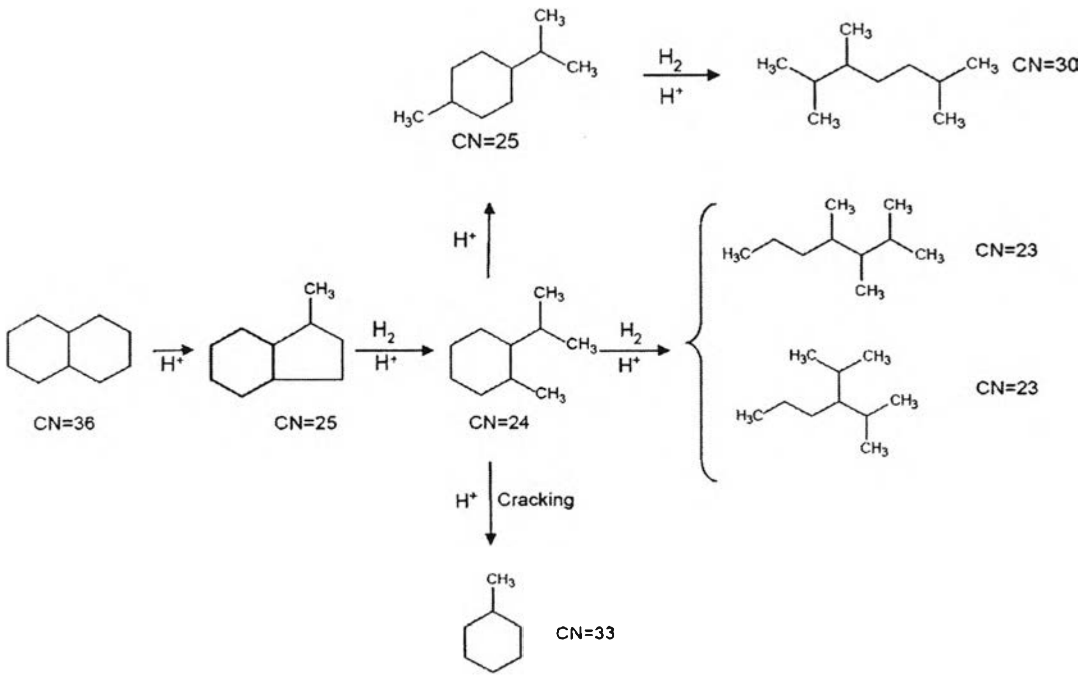


Figure 2.4 Predicted cetane numbers of intermediates and products of the reaction pathway of acid-catalyzed ring opening of decalin (Santana *et al.*, 2006).

Table 2.1 Predicted cetane numbers of ring contraction products of the reaction pathway of acid-catalyzed ring opening of decalin (Santana *et al.*, 2006)

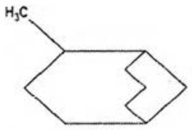
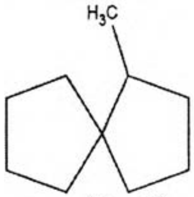
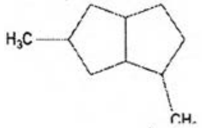
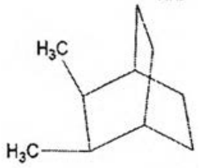
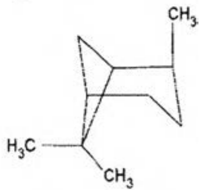
Name	Structure	Predicted CN
Methylbicyclo[3.3.1]nonane		22
2-Methyl-bicyclo[4.4]nonane		13
Dimethylbicyclo[3.3.0]octane		19
Dimethylbicyclo[2.2.2]octane		14
Trimethylbicyclo[3.1.1] heptane		11

Table 2.2 Predicted cetane numbers of ring opening products of the reaction pathway of acid-catalyzed ring opening of decalin (Santana *et al.*, 2006)

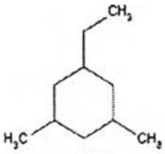
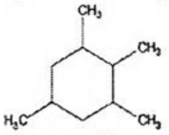
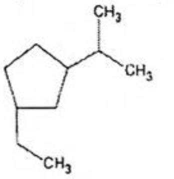
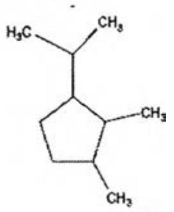
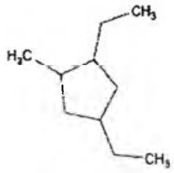
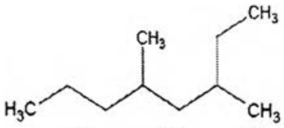
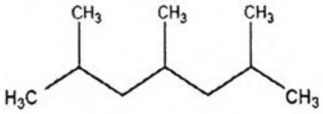
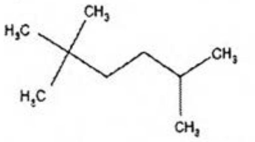
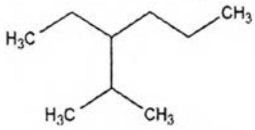
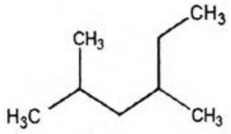
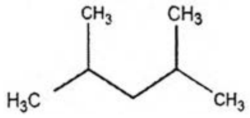
Name	Structure	Predicted CN
1-Ethyl-3,5-dimethylcyclohexane		30
1,2,3,5-Tetramethylcyclohexane		18
1-Ethyl-3-(methylethyl) cyclopentane		29
1,2-Dimethyl-3-(methylethyl)cyclopentane		15
1,3-Diethyl-5-methylcyclopentane		28

Table 2.3 Predicted cetane numbers of alkane products of the reaction pathway of acid-catalyzed ring opening of decalin (Santana *et al.*, 2006)

Name	Structure	Predicted CN
2-Ethyl-4-methylheptane		39
2,4,6-Trimethylheptane		44
2,2,5-Trimethylhexane		29
3-Ethyl(2-methyl)hexane		36
2,4-Dimethylhexane		32
2,4-Dimethylpentane		29

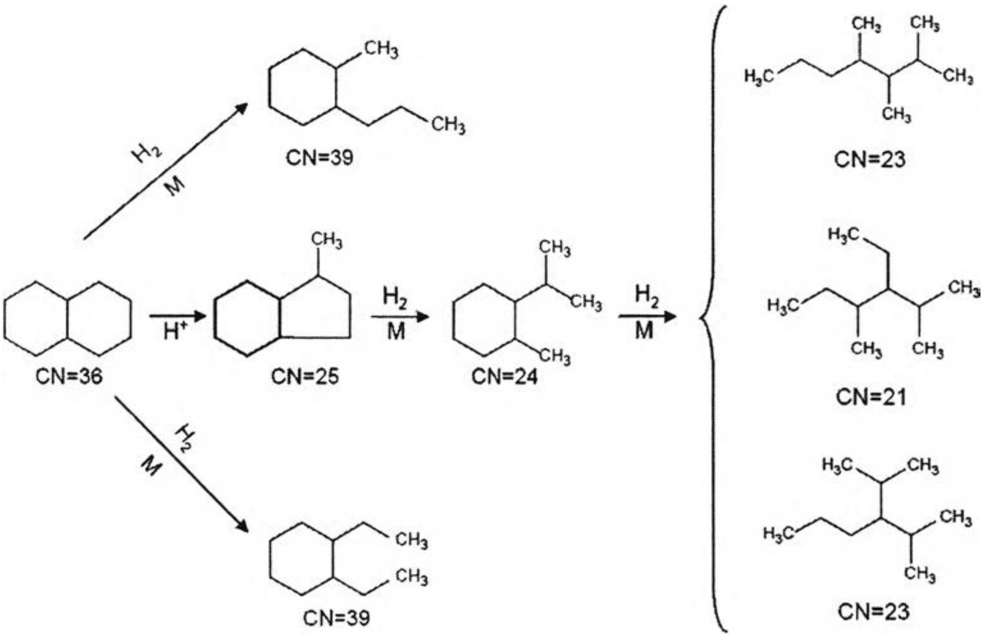


Figure 2.5 Predicted cetane numbers of intermediates and products of the reaction pathway of metal-catalyzed ring opening of decalin via dicarbene mechanism (Santana *et al.*, 2006).

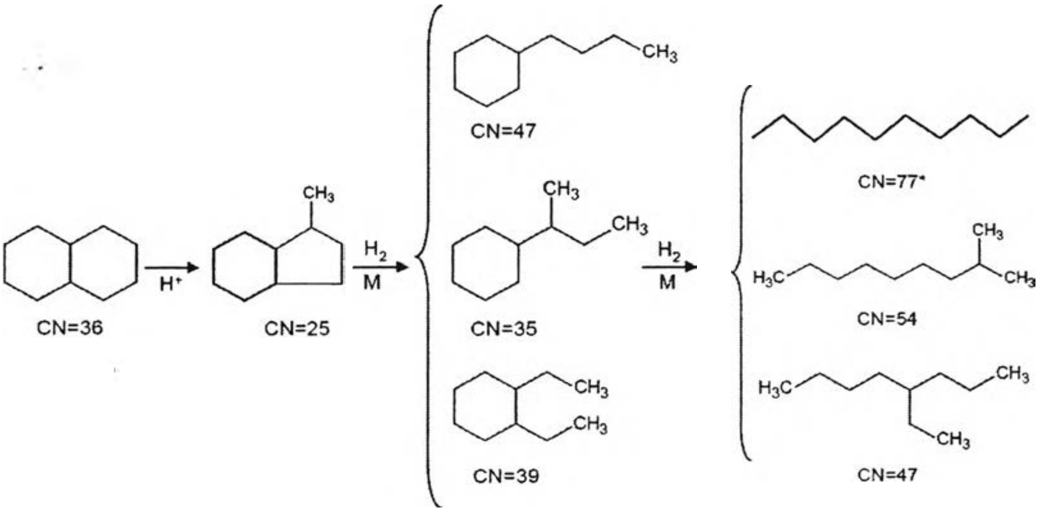


Figure 2.6 Predicted cetane numbers of intermediates and products of the reaction pathway of metal-catalyzed ring opening of decalin via substituted C-C bond cleavage mechanism (Santana *et al.*, 2006).

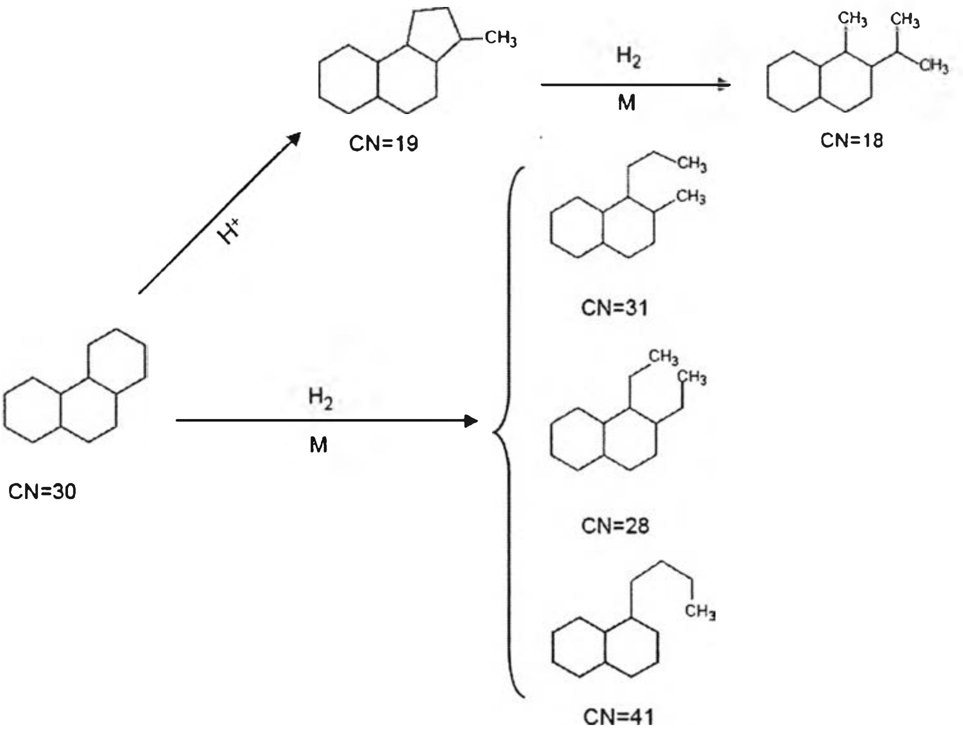


Figure 2.7 Predicted cetane numbers of intermediates and products of the reaction pathway of the opening of one ring of perhydrophenanthrene.

Although the ring opening may result in insignificant cetane number improvement, the volume gain can be considered as the other potential benefits as shown in Figure 2.8.

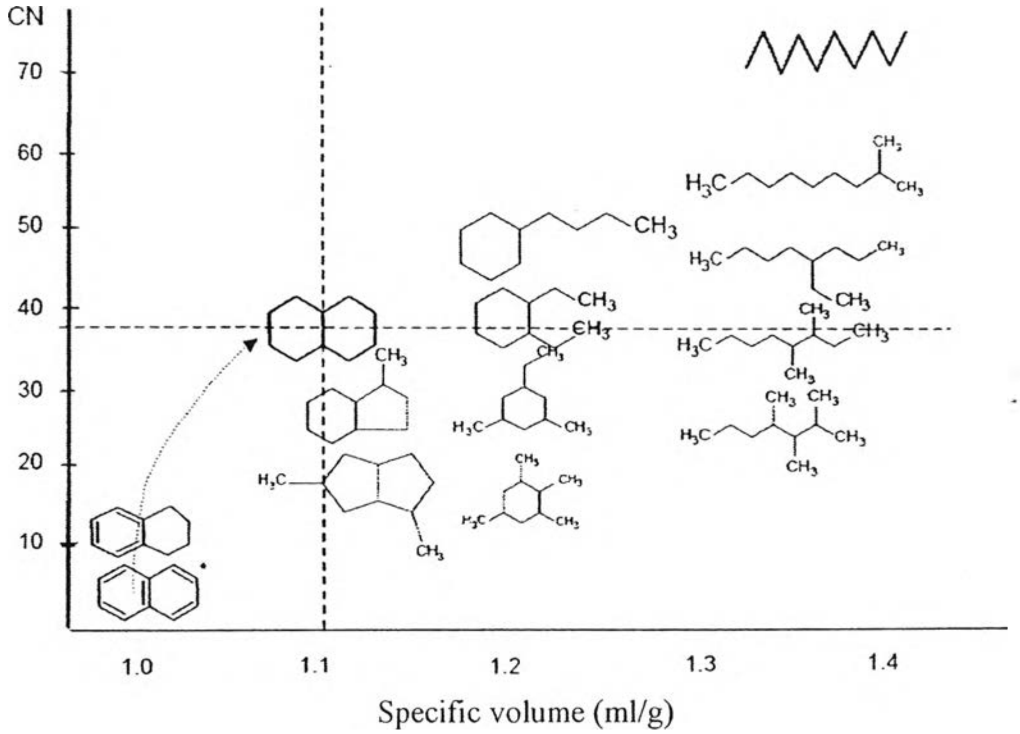


Figure 2.8 Cetane number and specific volume of typical products of selective ring opening (Santana *et al.*, 2006).

2.5.3 Prediction of Octane Number from Ring Opening Products

Even though most of the ring opening research is focused mainly on the products with high cetane number, the same concept, interestingly, can also be applied in octane number improvement. Unlike diesel fuel, the saturation of aromatics to naphthenic molecules dramatically decreases the octane number in gasoline. Thus, the ring opening of the naphthenic ring is required since the octane number of some of the ring opening products provide higher octane number compared to that of naphthenes. It was noticed that in order to obtain high octane number, only the ring opening products from the cleavage of the C-C bond at unsubstituted positions are required while the products from the cleavage at the substituted position ended up with low branched chain hydrocarbons which remarkably decrease in octane number.

In some previous works, the prediction of octane number of gasoline mixtures was focused on (Albahri *et al.*, 1995 and Billingsley *et al.*, 1995). It is generally known that the octane number of the blending hydrocarbons have an octane number quite different from that of either component, even though the two components are of equal octane number. Significant deviations from linearity were found in a blend of paraffins and olefins (Ghosh *et al.*, 2006). Deviations due to nonlinear interactions among different hydrocarbons group (i.e. paraffins, olefins, aromatics, etc.) is even significantly different. Especially, in a mixture containing more than two compounds, this system becomes even more complicated. Recently, an improved model from experiment on the research octane number (RON) and motor octane number (MON) data of 1471 gasoline fuels was created (Ghosh *et al.*, 2006). Interaction parameters were obtained between large groups of molecules (i.e. between paraffins and olefins, etc.) in order to minimize the number of calculations. This technique proved to be quite accurate, with a standard error of approximately 1 for the prediction of both RON and MON of fuel mixtures. The equation developed can be readily applied as:

$$ON = \frac{\sum\limits_{PONA} v_i \beta_i ON_i + \left(\dfrac{k_{PN}^{(a)} v_n + k_{PO}^{(a)} v_O}{1 + k_{PN}^{(b)} + k_{PO}^{(b)} v_O} \right) \sum\limits_{P} v_i \beta_i ON_i}{\sum\limits_{PONA} v_i \beta_i + \left(\dfrac{k_{PN}^{(a)} v_n + k_{PO}^{(a)} v_O}{1 + k_{PN}^{(b)} + k_{PO}^{(b)} v_O} \right) \left(\sum\limits_{P} v_i \beta_i - \sum\limits_{P} v_i \right)} \qquad (1)$$

where v_i is the volumes fraction of the ith component used;

β_i is the blending values of the ith component;

ON_i is the octane number of the pure component;

k_{PO} is the interaction parameters between paraffins and olefins; and

k_{PN} is the interaction parameters between paraffins and naphthenes.

All molecules are divided into four groups: paraffins (P), olefins (O), naphthenes (N), and aromatics (A). The average value of the parameters, grouped by P, O, N and A, are reported in Table 2.4. Based on this equation, and knowing the composition and pure octane numbers of a fuel mixture, an estimation of the blending ON may then be made.

Table 2.4 Parameters value for octane number calculation (Ghosh *et al.*, 2006)

molecular class	molecular lumps	β(RON)	β(MON)
n-paraffins	nC_4–nC_{12}	2.0559	0.3092
i-paraffins	C_4–C_{12} mono-, di-, and trimethyl-*i*-paraffins	2.0204	0.4278
naphthenes	C_5–C_9 naphthenes	1.6870	0.2821
aromatics	benzene–C_{12} aromatics	3.3984	0.4773
olefins/cyclic olefins	C_4–C_{12} linear, branched, and cyclic olefins	8.9390	10.0000
oxygenates	MTBE, EtOH, TAME	3.9743	2.0727
interaction parameters	$k_{PN}^{(a)}$, $k_{PN}^{(b)}$, $k_{PO}^{(a)}$, $k_{PO}^{(b)}$	0.2, 2.4, 0.4, 3.6	0.2, 2.4, 0.4, 3.6