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Evaluation of different reaction strategies for the improvement of cetane number in diesel fuels

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Abstract

Cetane number improvement of diesel fuels is a difficult task that refiners will face in the near future. Aromatics saturation by deep hydrogenation is a necessary, but perhaps not sufficient step in the diesel treatment. Some researchers have proposed selective ring opening (SRO) as an additional step in the upgrading. In this work, we explore some possible reaction pathways of compounds typically found in diesel after different levels of hydrogenation, i.e. decalin (decahydronaphthalene), perhydrophenanthrene, tetralin (1,2,3,4-tetrahydronapthalene), as well as 1-ring and 2-ring aromatic phenanthrenes. We have estimated the cetane number (CN) of each individual compound involved in the reaction pathways, using an artificial neural network program that was trained with pure compound cetane numbers from a database. The results demonstrate the great challenge that reaching high CN represents. In the conversion of decalin, acidic catalysts alone are not able to yield products with CN significantly higher than the decalin feed. Similarly, no significant gain in CN can be expected with hydrogenolysis metal catalysts operating via the dicarbene mechanism. Only in the case of selective metal-catalyzed hydrogenolysis, with preferential cleavage at substituted C–C bonds, the predicted products have CN substantially higher than the decalin feed. As expected, branching has a strongly negative effect on the CN and it should be minimized. Both, metal-catalyzed di-carbenium C–C cleavage and acid-catalyzed ring contraction/ring opening combination leave branching groups in the product. Similarly, the acid-catalyzed ring opening of perhydrophenanthrene does not result in a significantly higher CN than the initial feed. The possibility of minimizing hydrogen consumption in the CN improvement process by an initial partial hydrogenation followed by ring opening was tested by using phenanthrene and tetralin as probe molecules. In the first reaction strategy, partially hydrogenated phenanthrenes (1-ring and 2-ring aromatics) were followed by ring opening of one of the saturated rings. Although this option would lead to lower overall hydrogen consumption, it results in products of much lower CNs than the ones obtained by full hydrogenation of phenanthrene. Similar results are obtained for tetralin. From this analysis, it is clear that upgrading CN of diesel requires extensive hydrogen consumption. For further upgrading, highly selective hydrogenolysis catalysts are needed in order to minimize branching and therefore obtain high CN products.

Keywords: Cetane number; Neural networks; Aromatics; Diesel; Ring opening; Ring contraction

1. Introduction

Recent environmental legislation on diesel fuels focuses on sulfur content, polynuclear aromatics (PNA), and cetane number (CN). To meet these regulations, several approaches have been proposed. One approach for improving CN is to use compounds known as ‘cetane boosters’. These compounds, frequently organic nitrates, improve cold-start performance, reduce combustion noise, and may reduce particulate matter (PM) emissions [1–4]. But, at the same time, cetane boosters increase the flammability of the fuel, are potentially more hazardous due to ultrafine particle emissions [5], and degrade the storage stability of the fuel. As another alternative, in cases where it is available, blending with Fischer–Tropsch (FT) gas-to-liquids diesel fuel results in increased CN and reduced concentrations of aromatics, sulfur, and other impurities [6]. However, extensive blending with FT may not be an economically viable solution [7]. A third option to reach higher CN while simultaneously reducing aromatics is further upgrading of the petroleum stream by deep

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Nomenclature

ANN	Artificial neural network	MLP	Multilayer perceptron neural network
ANN1	Artificial neural network trained with paraffins, isoparaffins, and cycloparaffins	PE	Processing Element
ANN2	Artificial neural network trained with olefins and aromatics	NMSE	normalized mean square error
CN	Cetane number	PHYPHE	Perhydrophenanthrene
DCN	Derivative Cetane Number (Cetane number measured by ASTM D6890-03a)	PM	Particulate matter
IQT™	Ignition Quality Tester	PNA	Polynuclear aromatic
LCO	Light cycle oil stream	RC	Ring contraction products
		RO	Ring opening products
		SRO	Selective ring opening

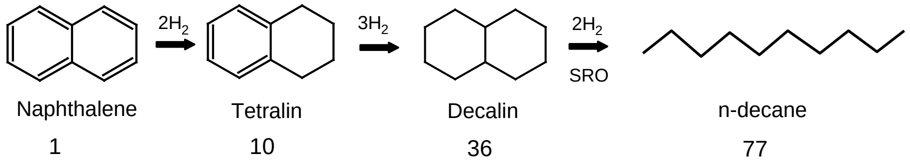
hydrotreating [8–13]. The resulting CN greatly depends on the nature of the crude as well as the refinery blending strategies. For example, the incorporation of light cycle oil (LCO) as part of the diesel pool has a negative impact on CN, mainly due to its high aromatic content. Even after deep hydrogenation, the expected high-CN regulations may not be met, so further upgrading is needed [14–17]. Some researchers have suggested that a combined hydrotreating/selective ring opening (SRO) process is a potential solution for significantly improving CN beyond what can be obtained with hydrogen saturation alone [18–22]. As shown in Scheme 1, the conversion of naphthalene to *n*-decane results in a CN increase from 1 to 77. However, it is not obvious how one can convert the PNA into an *n*-paraffin. As we show below, the most likely products are isoparaffins and only a few of them can result in a CN higher than that of the feed. It is therefore important to evaluate the possible reaction paths and the CN of each resulting product to determine what catalysts could be most efficient in this task.

In this study, we have used the software MDL®QSAR (from MDL Information Systems, Inc.) to calculate molecular descriptors and developed artificial neural networks (ANNs) to predict the cetane number of individual components. Molecular descriptors are quantitative properties that allow us to obtain conformational, electronic, molecular shape, quantum mechanical, spatial, structural, thermodynamic, and topological information of molecules. ANNs have been previously used to estimate the CN of diesel fuel [23–25]. In this work, we have focused on pure compounds to allow us to investigate specific reactions. Therefore, the training set for the ANNs comes from a vast compendium of cetane number values of pure compounds. With this tool, we have been able to predict the CN of the products of different reaction pathways in the conversion of several diesel fuel components. In particular, decalin (decahydronaphthalene), perhydrophenanthrene, 1-ring and 2-ring aromatic phenanthrenes, and tetralin (1,2,3,4-tetrahydronapthalene) have been used as starting compounds. The purpose of this study is to discuss and evaluate possible reaction strategies to maximize CN in diesel fuel. This analysis has also allowed us to assess strategies that have been proposed in the literature, but have not been previously tested.

2. Cetane number estimation

Artificial neural networks are highly distributed interconnections of adaptive nonlinear processing elements (PEs) [26]. An ANN is a set of interrelated PEs divided into layers (input layer, one or more inner layers, and an output layer). The connection strengths, also called the network weights, can be adapted such that the network's output matches a desired response. So, given a training set, ANNs can identify correlation patterns among inputs and outputs [27,28]. ANNs have found applications in the area of data mining and forecasting among other fields [29,30]. ANNs have also been used to predict the octane number of gasolines [31], and as mentioned above, cetane number of diesel fuels [23,25,32].

In the present work, we have estimated the CN of individual components of diesel fuel with ANNs built with the software NeuroSolutions® 4.32 (from NeuroDimension Inc.). The initial database obtained from Murphy et al. [33] is shown in Appendix 1 and consists of experimentally measured CN values of 147 hydrocarbons classified as *n*-paraffins, isoparaffins, cycloparaffins, olefins, and aromatics. It is important to point out that, due to the diverse sources of CN in the database, the error in the CN of individual compounds in this database can be fairly high. For example, the ASTM D-613 presents an uncertainty



Scheme 1.

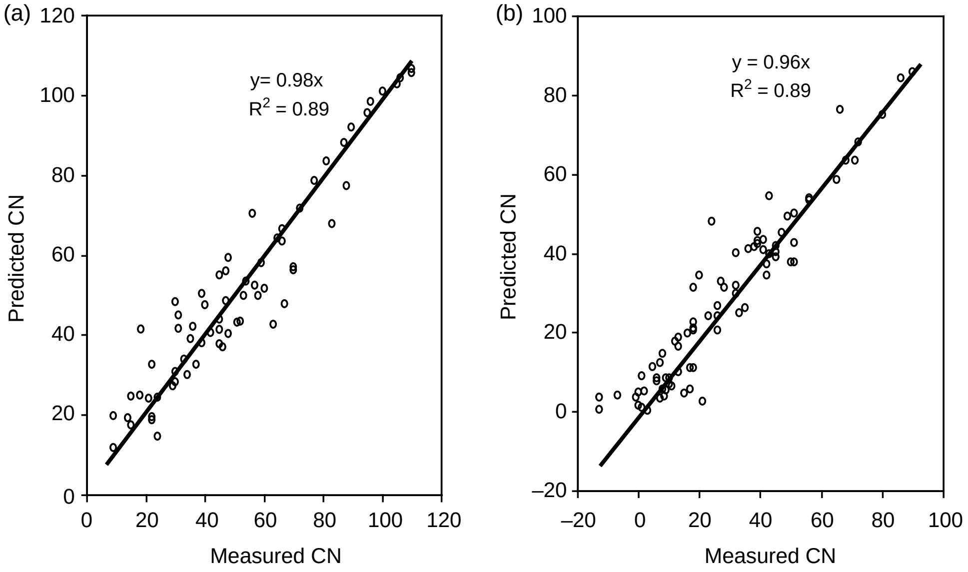


Fig. 1. (a) Quality of model prediction using artificial neural networks for paraffins, isoparaffins, and cycloparaffins. (b) Quality of model prediction using artificial neural networks for olefins and aromatics.

(reproducibility limits at the 95% acceptance level) that varies from 2.8 (for CNs around 40) to 4.8 (for CNs around 56) [33].

Other prediction methods have been used. For example, a correlation between CN and CH_3/CH_2 group ratio has been found [35]. However, the results of this prediction have a greater uncertainty than those found with our method. Group contribution methods can be used for predicting octane numbers (RON or MON) and they could also be applicable to CN if a correlation is used to convert octane numbers to CN. In fact, we have applied this group additivity method followed by a crude correlation of MON vs. CN and the results were much worse than those obtained from the present method. Apart from the accuracy of the method employed in the prediction of CN, the major source of error is the database itself, which not only includes the intrinsic error of the CN determination, but also includes error arising from the diversity of the sources. For example, some of the values reported in the database were estimated using a different scale (cetene numbers that were later converted into CN scale), others were estimated from blends, and some others were obtained using different test methods. Also, some data were obtained a long time ago and the low purity of the compounds used in those measurements could be another source of error. Despite these limitations, it is important to emphasize the value of the data presented in the database because it not only contains the most comprehensive data of pure compound CN values available in the published literature, but also because most CN values are consistent with known trends for CN. For example, for *n*-paraffins the CN increases with carbon number. Also, at the same carbon number, isoparaffins present lower CN than *n*-paraffins, and in general aromatics have a much lower CN compared to other groups.

Molecular descriptors of the individual molecules were used as input for the ANNs. A total of 99 molecular descriptors were calculated for each compound using the software MDL®QSAR. In order to reduce the number of inputs to a more manageable number, we used the software XLSTAT-Pro® 7.5 (from Addinsoft) to obtain the correlation matrix of the parameters. This analysis allowed us to determine what parameters have the greatest influence on the CN prediction. Several options were tested. We found that it was most effective to divide the 147 hydrocarbons into two subgroups. The first group consists of paraffins, isoparaffins, and cycloparaffins and the second group consists of olefins and aromatics. For the first group of compounds, the most influential parameters were found to be maxhp, Ovality, Gmin, xpc4, and SssCH2_acnt. These descriptors are defined as follows: maxhp is the highest positive charge in the hydrogen atom; Ovality of the molecule is defined as (molecular surface area)/($4\pi R^2$), where $R=(3\text{ molecular volume}/4\pi)^{1/3}$; Gmin is the minimum *E*-state value in the molecule, which quantifies electron accessibility; Xpc4 is a molecular connectivity Chi index and accounts for the branching of the molecule; SssCH2_acnt is a count of the number of $–CH_2–$ groups in the molecule. For olefins and aromatics, the parameters chosen were maxhp, Ovality, ka3, phia, and $SssCH_2$. Here, ka3 and phia are Kappa Alpha Shape indices that contain shape information, and SssCH2 is an electro-topological state (*E*-State) index for $–CH_2–$ groups, which quantifies the electron accessibility at each structural component of the molecule being described.

Table 1
Comparison between derived cetane number (DCN) obtained using an ignition quality tester and cetane number predicted by the artificial neural network trained with paraffins, isoparaffins, and cycloparaffins data

Name	DCN	Predicted CN
2-Methyl-heptane	47	47
3-Methyl-heptane	45	43
n-Butyl-cyclohexane	47	46
1,3,5-Trimethyl-cyclohexane	31	28
Decalin	33	36

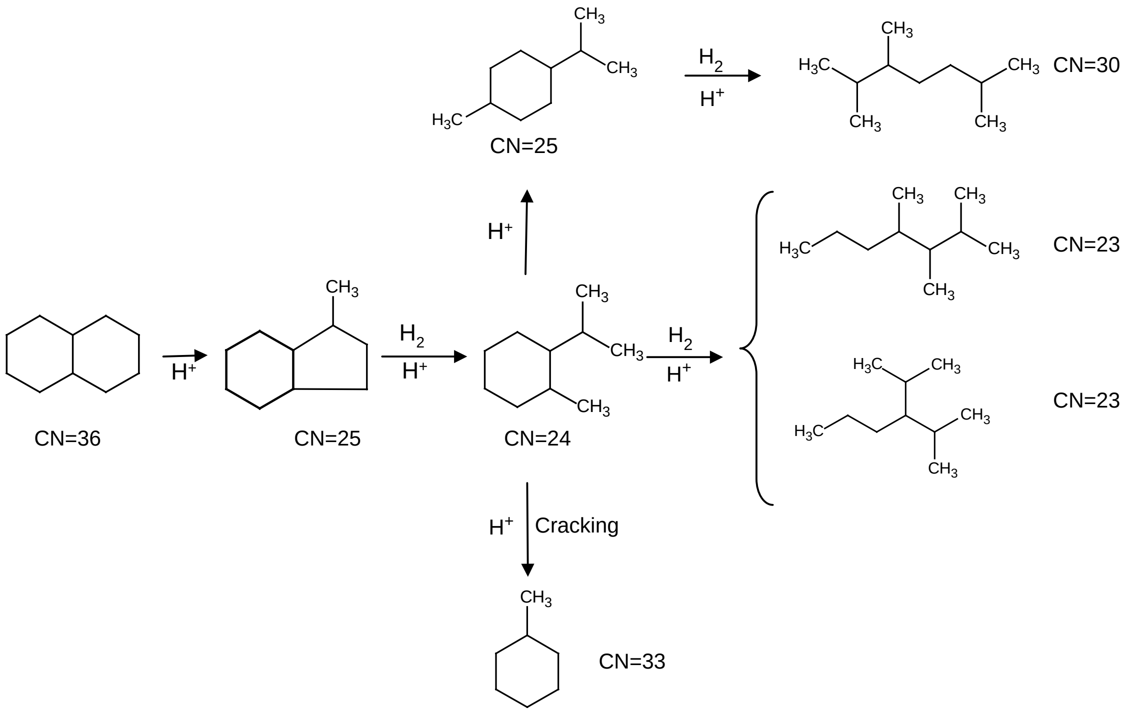


Fig. 2. Cetane number of intermediates and products of the reaction pathway of acid-catalyzed ring opening of decalin.

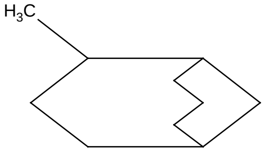
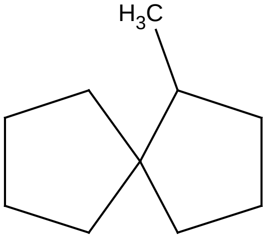
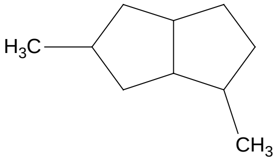
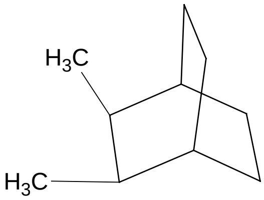
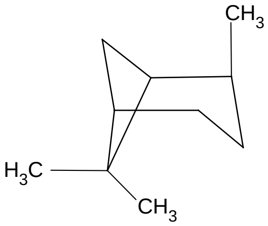
The training set for each ANN consisted of 80% of the available data for each group. The other 20% were used for cross-validation. Further validation of the ANNs was carried out with a small set of 'derived cetane number' (DCN) values measured experimentally by our group with an Ignition Quality Tester (IQT™) following ASTM D6890-03a. It has been shown that the DCN corresponds well with the cetane number measured by engine ASTM D613 [34]. All 11 types of ANN models available in NeuroSolutions 4.32® software were tested. Accuracy of the prediction varied according to the type of ANN. Within the same type of ANN, several configurations were tested. The most common variables changed in the configuration of an ANN were the number of inner layers and PEs of each layer. However, simplicity is paramount in the design of our configurations because although ANNs prediction power increases with the number of layers and the number of PEs, an increased number of variables also means an increased number of weights. It is widely accepted that, in order to obtain a network that can be reliably used for prediction, the number of inputs required for training the network should be at least twice the number of weights [26].

In our first attempt, we tried to treat with only one neural network the entire set of hydrocarbons. However, we later found that two separate correlations (one for paraffins, cycloparaffins, and isoparaffins and one for olefins and aromatics) worked much better. There is some justification for this separation based on our understanding of combustion chemistry. The rate determining step for paraffin ignition in this temperature range is hydrogen abstraction. However, for unsaturated compounds such as olefins and aromatics, there is a resonance-stabilized free radical after the initial H-abstraction. Since the two sets of compounds have very different key reaction steps, it is not unexpected that separate correlations would work better than one correlation that tries to capture all the subtleties. Specifically, for paraffins, isoparaffins, and cycloparaffins the ANN (indicated as ANN1 in the rest of the text) with the lowest normalized mean squared error (NMSE) was the multilayer perceptron (MLP) trained with backstatic propagation. ANN1 had one inner layer with three PEs. The NMSE was 0.093 and the standard error was eight cetane numbers. Fig. 1(a) shows a comparison of the experimental CN values with the values predicted by ANN1. There are some outliers, but the quality of the agreement is reasonably good if one takes into account the intrinsic error of the data used to train ANN1. Table 1 shows a comparison between DCN measured experimentally by our group and the CN predicted by ANN1. One of the reasons for such good agreement could be due to the fact that MLP neural networks handle outliers better than the traditional statistical methods. For the group comprised of olefins and aromatics, the ANN (indicated as ANN2) with the lowest NMSE (0.096) was an MLP that had one inner layer and 4 PEs. The comparison of the experimental CN values with the values predicted by ANN2 is shown in Fig. 1(b). The standard error was eight cetane numbers.

3. Approach

As shown in Scheme 1, the hydrogenation of PNA results in a drastic increase in CN, going from 1 to 36 when naphthalene is completely hydrogenated. However, this increase might not be sufficient and therefore in recent publications it has been proposed that SRO can lead to further increases in CN. This conclusion may come from the assumption that normal

Table 2
Cetane number of ring contraction products of the reaction pathway of acid-catalyzed ring opening of decalin

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

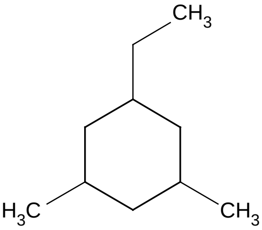
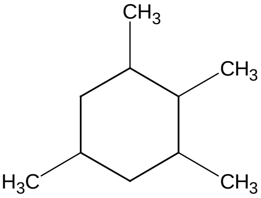
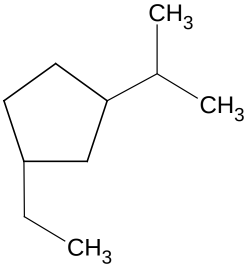
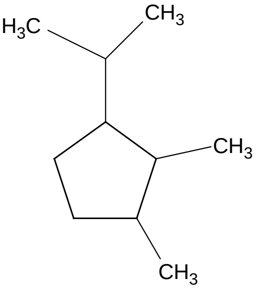
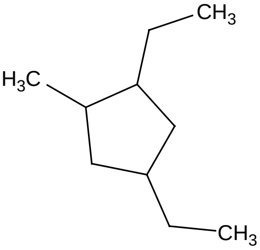
and iso-paraffins should have much higher CN than the corresponding naphthenic molecules. However, it is not obvious that most isoparaffins resulting from ring opening will have higher CN. To test the proposed strategy, we have used the ANN1 and ANN2 neural networks described in the previous section to examine the CN of the possible products of different reaction pathways of SRO. We have selected molecules that are typically found in diesel fuels as representative reactants and evaluated the CN of the product streams. Various possible reaction pathways were considered in order to gain insight into which strategy should be pursued to maximize CN in the case of C10–C14 molecules containing 6-membered and 5-membered rings. The opening of the ring can be accomplished with either acid (e.g. HY zeolites) or metal (e.g. group VIII) catalysts, or even a combination of both. In this work, we have calculated the CN of the various products of the typical reaction pathways occurring over both acidic and metal catalysts. Also, we have included tables with the CNs for other possible products that could be present [18, 22]. For consistency, all CN values presented in this work were estimated using either ANN1 or ANN2.

4. Results and discussion

4.1. Acid-catalyzed ring opening of decalin

Decalin is the fully hydrogenated product of naphthalene and it has been frequently used as a probe molecule to study SRO. Fig. 2 shows the CN of some possible products of decalin SRO over an acidic catalyst. Here, as found by Kubicka et al. [18] as well as by our own group [16], decalin first undergoes a ring contraction (RC) step followed by ring opening (RO). The RC is a typical carbocation reaction that can be originated by either protolytic cracking [20] or through the formation of olefinic intermediates via hydrogen transfer [18]. Products from RC are alkyl-bicyclononanes and bicyclooctanes. Besides the RC compounds illustrated in Fig. 2, additional RC products along with their respective CN are listed in Table 2. The results of this analysis indicate that, even when keeping the same carbon number in the molecule, the generation of an increased number of methyl groups in the molecular structure decreases the CN. This decrease with increasing CH_3/CH_2 ratio has been previously reported [35]. As experimentally demonstrated [16],

Table 3
Cetane number of ring opening products of the reaction pathway of acid-catalyzed ring opening of decalin

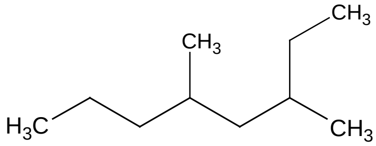
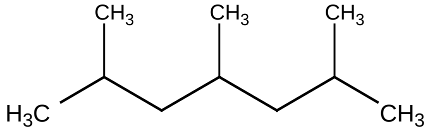
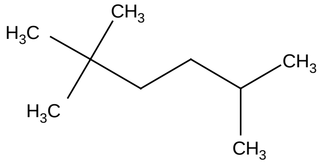
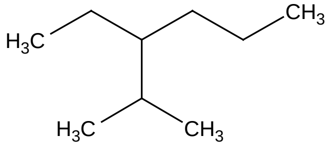
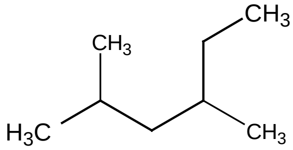
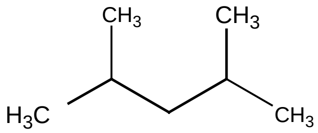
Name	Structure	Predicted CN
1-Ethyl-3,5-dimethylcyclohexane		30
1,2,3,5-Tetramethylcyclohexane		18
1-Ethyl-3-(methylethyl)cyclopentane		29
1,2-Dimethyl-3-(methylethyl)cyclopentane		15
1,3-Diethyl-5-methylcyclopentane		28

it is easier to open the C5 rings in RC compounds than the C6 rings in decalin. As a result, as conversion increases, the reaction proceeds from RC products to RO products containing a C6 ring attached to alkyl groups, which result from the opening of the C5 ring.

Accordingly, to generate the RO products shown in Fig. 2, we have considered that following the RC, the opening of one ring is mainly accomplished by β-scission of the 5-membered ring and hydrogenation of the resulting olefin. It can also be expected that some compounds undergo methyl shift [16]. This shift is illustrated with the methyl shift of the product of the first ring opening in Fig. 2 (top path). The CN of other one-ring-opening products, alkylcyclohexanes and alklylcyclopentanes, is presented in Table 3. From Tables 2 and 3 an important conclusion can be drawn. That is, if only one ring is opened on acidic catalysts, the final products will not have significantly higher CN than the initial feed. This limitation has been previously recognized by McVicker et al. [21].

One can therefore, conclude that the opening of the second ring is needed to achieve higher CN. However, as illustrated on the right hand side of the scheme in Fig. 2, the opening of the second ring by itself is not a guarantee of high CN. For example, over an acidic catalyst that would open the second ring via a typical β-scission, this reaction would yield the type

Table 4
Cetane number of alkane products of the reaction pathway of acid-catalyzed ring opening of decalin

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

of highly branched isoparaffins shown in Fig. 2. The CN of some other representative products resulting from opening of the second ring are presented in Table 4. Fig. 2 and Table 4 show that second ring-opening products obtained over an acidic catalyst may give rise to some products with higher CN than the first ring-opening and the initial RC products, but most of them (seven out of nine compounds) have the same or even lower CN than that of the feed. Also the unavoidable cracking that accompanies all acid-catalyzed reactions would result in a substantial loss of original molecular weight and a lower CN than the original feed.

5. Metal-catalyzed opening of C5 and C6 rings

Given the limitations of acid catalysts for improving CN, we focused on the use of metal catalysts with high hydrogenolysis activity. In this section we have evaluated the possibility of using metal catalysts for the opening of the first and second rings. Noble metals such as Rh, Ir, and Ru, are well known for being active hydrogenolysis catalysts. They are particularly effective for opening five-member rings, but much less effective for opening six-member rings. On metals as well as on acid catalysts, a five-member ring opens much faster than a six-member ring. For example, McVicker et al. [21] have shown that while alkylcyclopentanes can be readily ring-opened by low temperature hydrogenolysis over noble metals such as Ir, the corresponding ring opening of alkylcyclohexanes is almost a hundred times slower. They have proposed the addition of a mild acidity function to provide the catalyst the necessary ring-contraction activity without significant cracking. Therefore, we have evaluated the ring opening of both C6 and C5 rings under the assumption that they can occur after an RC step.

Hydrogenolysis of naphthenic rings on metals can proceed by different mechanisms. The most common hydrogenolysis mechanism that typically occurs on metals such as Ir and Rh is via the dicarbene intermediate. In this mechanism, the endocyclic C–C bond cleavage occurs on unsubstituted secondary C atoms [36]. On Pt, which has a much lower hydrogenolysis activity, other mechanisms may also be possible depending on the metal particle size. For example, Gault et al. [36] studied the effect of metal particle size in Pt/Al_2O_3 catalysts for the ring opening of methylcylopentane. They observed that on highly dispersed Pt/Al_2O_3, there was an equal chance of breaking any endocyclic C–C bond—a result that was attributed to a π-allyl mechanism that competes with

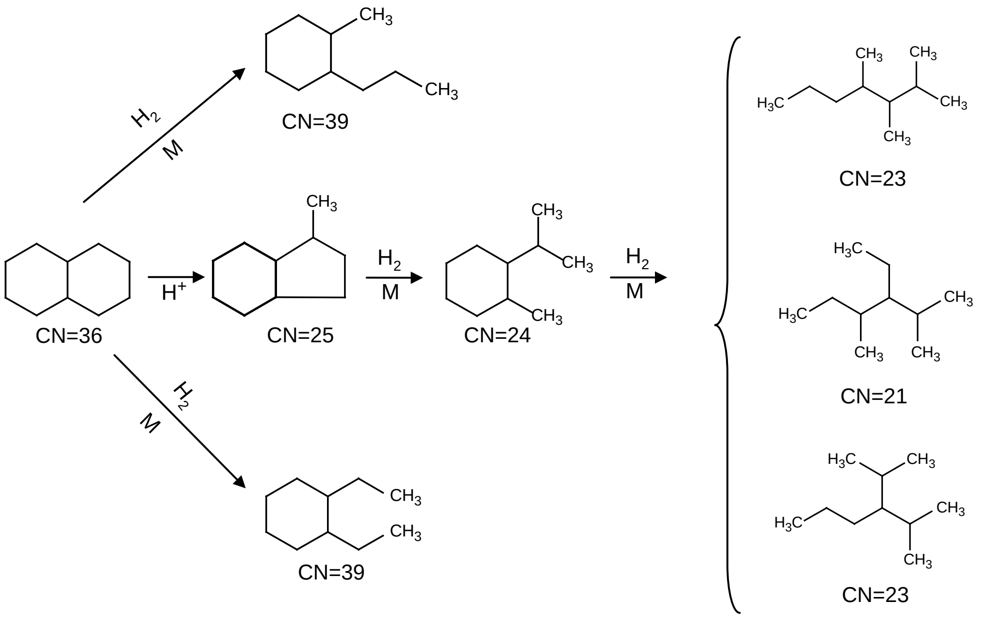
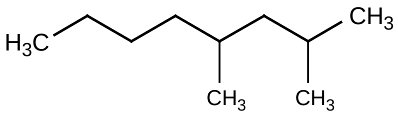
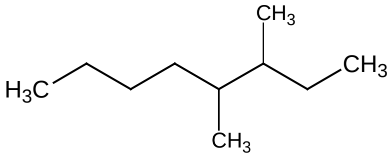
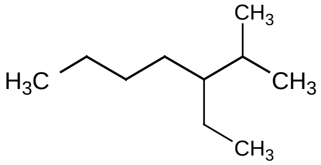
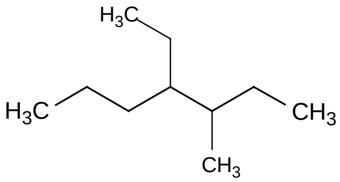
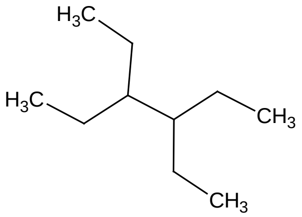


Fig. 3. Cetane number of intermediates and products of the reaction pathway of metal-catalyzed ring opening of decalin via dicarbene mechanism.

the dicarbene mechanism. This mechanism derives from π-absorbed-olefins that require a flat adsorption of three neighboring carbon atoms interacting with a single metal site on the catalyst surface. On the other hand, on Pt catalysts with larger metal particles, secondary–secondary C–C bonds were preferentially broken, according to the dicarbene mechanism mentioned above. In this case, unlike the π-allyl mechanism, two endocyclic carbon atoms are involved with two adjacent

Table 5
Cetane number of alkane products of the reaction pathway of bifunctional metal–acid catalyzed ring opening of decalin via dicarbene mechanism

Name	Structure	Predicted CN
2,4-Dimethyloctane		44
3,4-Dimethyloctane		39
3-Ethyl-2-methylheptane		39
4-Ethyl-3-methylheptane		37
3,4-Diethylhexane		34

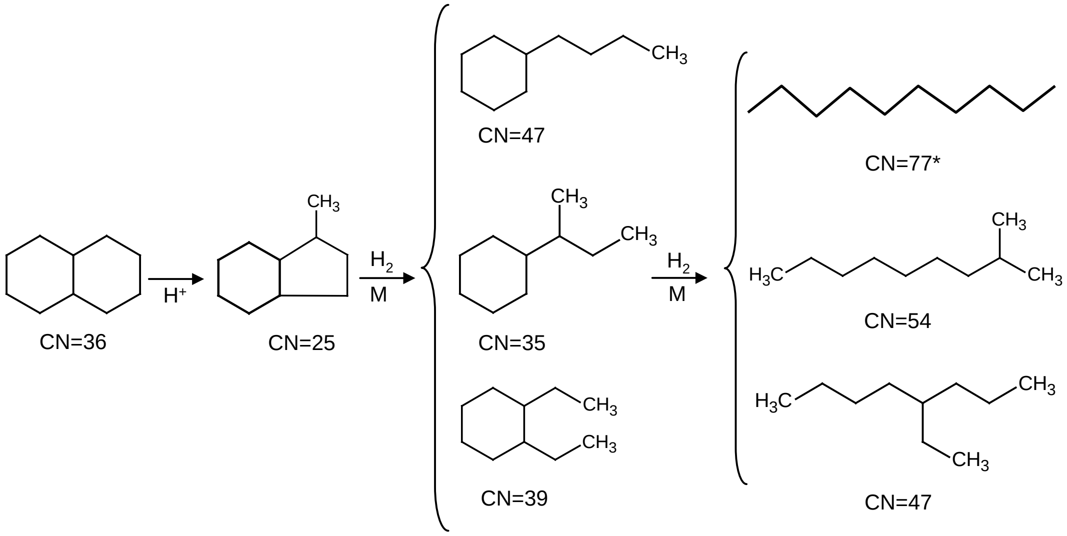
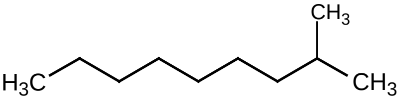
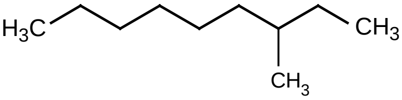
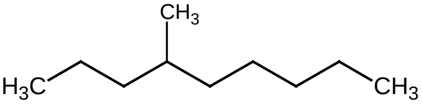
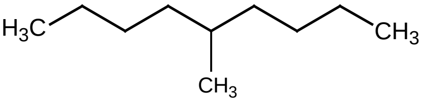
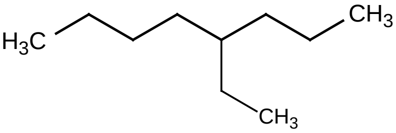


Fig. 4. Cetane number of intermediates and products of the reaction pathway of metal-catalyzed ring opening of decalin via substituted C-C bond cleavage mechanism.

metal atoms in the formation of the dicarbene intermediate. To explain the observed rupture of sterically-hindered substituted tertiary–secondary C–C bond on these low dispersed Pt catalysts, a third mechanism was proposed that competes with the dicarbene mechanism. This third mechanism involves a metallocyclobutane species as an intermediate and has higher activation energy than the dicarbene mechanism. In recent studies, both McVicker et al. [21] and Coq et al. [37] have cited the metallocyclobutane mechanism as responsible for the observed hydrogenolysis of 1,2,4 trimethylcyclohexane and 2,2,3,3-tetramethylbutane, respectively. We have evaluated the CN that would result when either the unsubstituted C–C (dicarbene) or substituted C–C bond cleavage occurs.

In the case in which the dicarbene mechanism is dominant, a reaction path like the one shown in Fig. 3 can be expected. In this figure we have only considered C–C cleavage of unsubstituted atom pairs for direct opening of C6 rings or C5 rings produced by a previous RC reaction. In contrast with previous expectations [21], no substantial gain in CN can be achieved by RO via dicarbene mechanism. From Fig. 3 and Table 5, it can be seen that the CNs of the second-ring-opened products obtained via the dicarbene mechanism are just slightly better than those obtained via the acid catalyzed reactions. This limited improvement is because the breaking of the unsubstituted secondary–secondary C–C bond still leads to products with a high degree of branching. Not only are these molecules

Table 6
Cetane number of alkane products of the reaction pathway of bifunctional metal-acid catalyzed ring opening of decalin via substituted C–C bond cleavage mechanism

Name	Structure	Predicted CN
2-Methylnonane		54
3-Methylnonane		48
4-Methylnonane		49
5-Methylnonane		50
4-Ethyloctane		47

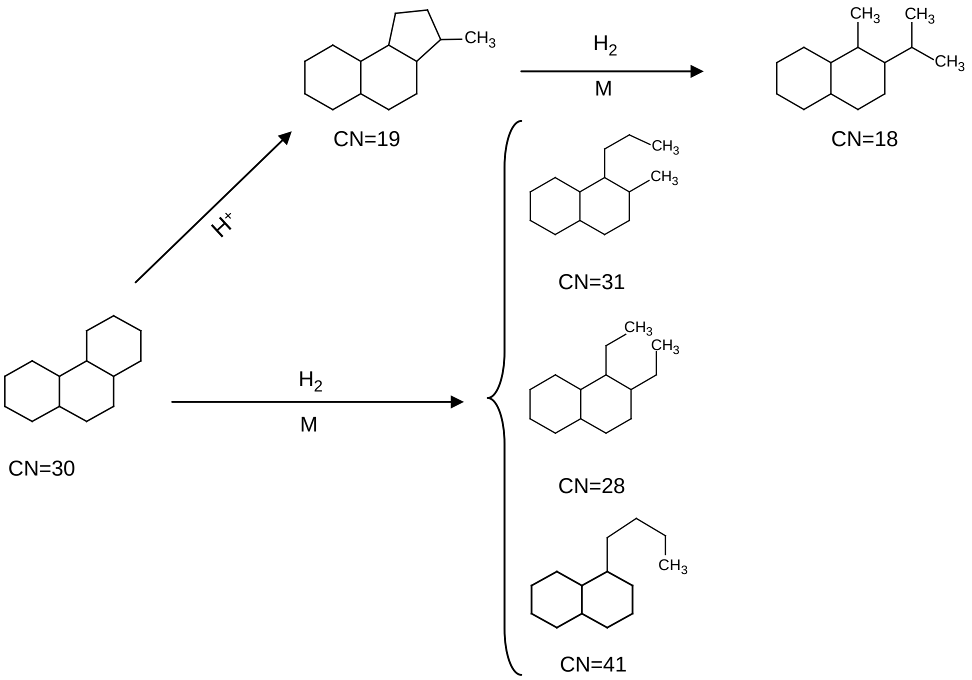


Fig. 5. Cetane number of intermediates and products of the reaction pathway of the opening of one ring of perhydrophenanthrene.

highly branched, but most branches are very short [21], in most cases just a methyl group. This is a disappointing result that weakens previous optimistic strategies, since the most active hydrogenolysis metal catalysts (Ir, Rh) operate primarily via the dicarbene mechanism.

Conversely, if the ring opening could take place on a catalyst that favors the breaking of substituted tertiary-secondary C–C bond and some of the even more sterically hindered tertiary–tertiary C–C bond, a typical reaction path might follow the scheme of Fig. 4. The CNs of these products are considerably higher than the ones obtained via either acid catalyzed or dicarbene mechanism. Actually, the CNs of every one of the second ring opening products presented in Fig. 4 and Table 6 are greater than the CN of the decalin feed. From this analysis, it can be concluded that the only successful strategy to significantly increasing CN of decalin feedstocks should be based on a precisely tailored catalyst with high selectivity towards the cleavage of substituted C–C bonds.

6. Ring opening of perhydrophenanthrene

Perhydrophenanthrene (PHYPHE) is the saturated product of phenanthrene, a major culprit for the formation of PM emissions in diesel exhaust [38]. The ring opening of perhydrophenanthrene is depicted in Fig. 5. Here, two possibilities are considered. The pathway shown on top corresponds to the acid-followed-by-metal catalyzed reactions. PHYPHE can first undergo ring contraction on a Bronsted site, and then the five-member ring can be opened by hydrogenolysis on a metal site. In this case, the product would have a CN significantly lower than the initial CN of PHYPHE. Since this route seemed to yield products with low CNs, another pathway was tested. In this second pathway, PHYPHE would directly react on the noble metal catalysts by hydrogenolysis of one the C6 rings. Accordingly, rupture of secondary–secondary C–C bonds and possibly tertiary–secondary C–C bonds can be expected. Only in the case of the severely sterically hindered cleavage of a substituted tertiary–secondary C–C bond, the product 1-butyl decalin results in a significantly higher CN than the starting naphthenic PHYPHE. From this, it can be concluded that (similar to the case of decalin) the opening of one ring of

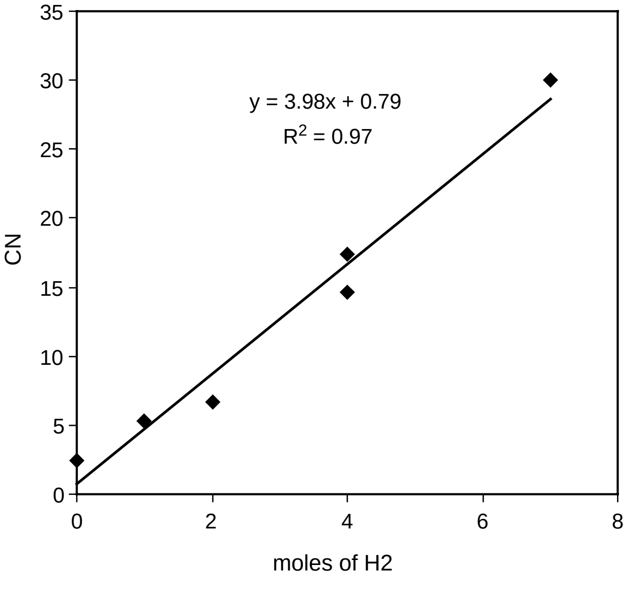


Fig. 6. Correlation of hydrogen consumption and cetane number improvement of products of hydrogenation of phenanthrene.

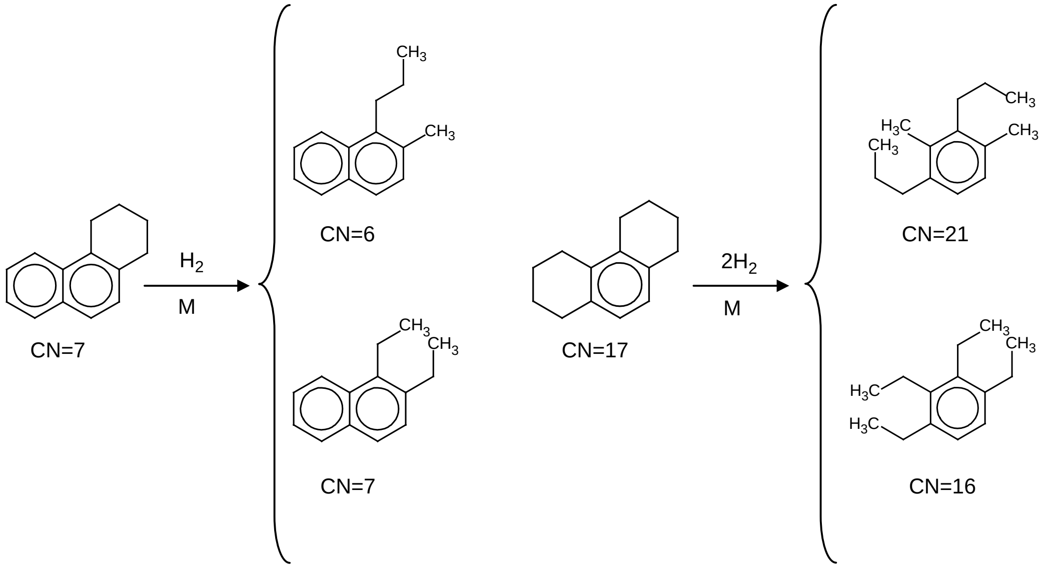


Fig. 7. Cetane number of products obtained through metal-catalyzed ring opening of 2 ring aromatics (2-R) and 1 ring aromatic (1-R) partially hydrogenated phenanthrenes.

PHYPHE would require an extremely selective catalyst in order to increase the CN.

7. Hydrogen consumption

New regulations to produce cleaner fuels are expected to greatly increase hydrogen demand in refineries [39]. This is particularly problematic in the upgrading of LCO, because extensive hydrotreating is needed to significantly improve the CN of the fuel. For example, to fully saturate a mole of naphthalene, five moles of H_2 are needed, resulting in a cetane improvement of 35 numbers (Scheme 1). Starting with phenanthrene, seven moles of H_2 are required to obtain the fully saturated compound, while the gain in cetane numbers according to Fig. 6 is 28 units. Fig. 6 describes the relationship between hydrogen consumption and CN improvement for phenanthrene. The amount of hydrogen consumed versus CN falls into a rather linear correlation. This trend is in good agreement with the results obtained by Wilson et al. [15] who reported similar behavior in the cetane improvement of hydrotreated distillates from synthetic crude.

One could expect to save in the total hydrogen consumed if partially hydrogenated products followed by SRO could result in cetane gains similar to those obtained by extensive hydrotreating. Unfortunately, as illustrated in Figs. 7 and 8, that is not the case. These figures show the results obtained for the SRO of partially hydrogenated products of phenanthrene and naphthalene, respectively. There is no net gain in CN for the SRO of the partially hydrogenated two-ring aromatic (Fig. 7). In the case of the 1-ring aromatic, no substantial gain in CN is achieved either. Similar results are seen in the case of SRO of tetralin, as shown in Fig. 8. Unfortunately, products that one could expect to yield a higher CN (for example *n*-butylbenzene) are not possible to obtain through ring opening because of the screening effect of the benzene ring [40]. From this analysis, it appears that ring-opening of partially hydrogenated compounds will not result in increased CN and severe hydrotreating cannot be avoided.

8. Fuel density and cetane number

Despite the low potential of SRO as a cetane improvement method, SRO of naphthenics may offer other potential benefits to refiners such as improvement in cloud point or volume increases observed when the naphthenic rings are opened. As shown in Fig. 9, complete hydrogenation greatly increases CN, but has only a minor effect on volume. Further volume increases can be achieved by SRO. However, this volume increase is accompanied by a substantial loss in CN if the SRO final product is highly branched. Therefore, a preferred

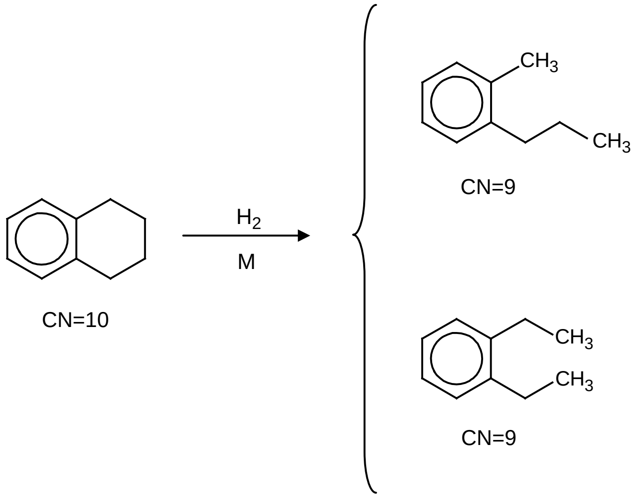


Fig. 8. Cetane number of products obtained through metal-catalyzed ring opening of Tetralin.

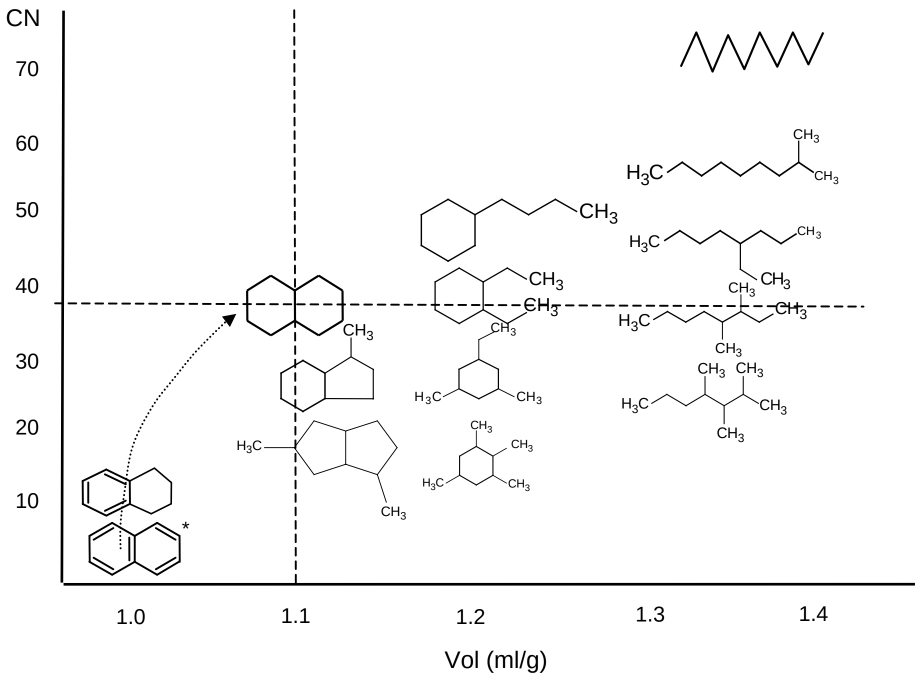


Fig. 9. Cetane number and specific volume of typical products of selective ring opening. *Naphthalene specific volume is at 373 K all others are at 293 K.

solution would be to selectively open the rings at substituted C–C bonds in order to increase volume without losing CN.

9. Conclusions

Improvement of CN of diesel is not a straightforward task. First, severe hydrotreating is needed. Otherwise, the ring opening of the partially hydrogenated products would lead to a dismal loss of CN compared to the CN of the fully hydrogenated molecules. In general, ring opening of only one ring of the fully hydrogenated products would not result in a substantial gain of CN compared to the initial CN of the fully hydrogenated molecule. Therefore, the opening of the second ring is crucial, but the catalyst employed to open the second ring must be extremely selective towards the rupture of substituted C–C bonds so branching is minimized and linear alkanes can be obtained. It is important to emphasize that unless a very selective catalyst is used, SRO leads to highly branched products with low CNs.

Acknowledgements

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Appendix A. Compilation of cetane number found in the literature by Murphy et al. [25]

(Table 7)

Table 7

Compound	CN
N-PARAFFINS	
n-Butane	22
n-Pentane	30
n-Hexane	45
n-Heptane	54
n-Octane	64
n-Nonane	72
n-Decane	77
n-Undecane	81
n-Dodecane	87
n-Tridecane	90
n-Tetradecane	95
n-Pentadecane	96
n-Hexadecane	100
n-Heptadecane	105
n-Octadecane	106
n-Nonadecane	110
n-Eicosane	110
ISOPARAFFINS	
2-Methylpentane	33
3-Methylpentane	30
2,3-Dimethylpentane	22
2,4-Dimethylpentane	29
2,2,4-Trimethylpentane	14
2,2,5-Trimethylhexane	24
2,2-Dimethyloctane	59
2,2,4,6,6-Pentamethylheptane	9
2,3,4,5,6-Pentamethylheptane	9
3-Ethyldecane	47
4,5-Diehtyloctane	20
4-Propyldecane	39
2,5-Dimethylundecane	58
5-Butylnonane	53
2,7-Dimethyl-4,5-diethyloctane	39
5-Butyldodecane	45

(*continued on next page*)

Table 7 (*continued*)

Compound	CN
7,8-Dimethyltetradecane	40
2,2,4,4,6,8,8-Heptamethylnonane	15
7-Butyltridecane	70
7,8-Diethyltetradecane	67
8-Propylpentadecane	48
9-Methylheptadecane	66
5,6-Dibutyldecane	30
9,10-Dimethyloctadecane	60s
7-Hexylpentadecane	83
2,9-Dimethyl-5,6-diisopentyldecane	48
10,13-Dimethyldocosane	56
9-Heptylheptadecane	88
9,10-Dipropyloctadecane	47
CYCLOPARAFFINS	
Cyclohexane	15
Methylcyclohexane	22
Ethylcyclohexane	45
n-Propylcyclohexane	52
trans-Decalin	46
Bicyclohexyl	51
3-Cyclohexylhexane	36
n-Propyldecalin	35
tert-Butyldecalin	24
sec-Butyldecalin	34
n-Butyldecalin	31
2-Methyl-3-cyclohexylnonane	63
n-Octyldecalin	31
4-Methyl-4-decalylheptane	21
1-Methyl-3-dodecylcyclohexane	70
3-Methyl-3-decalylnonane	18
2-Cyclohexyltetradecane	57
2-Methyl-2-decalyldecane	37
2-Methyl-2-cyclohexaylpentadecane	45
1,2,4-Trimethyl-5-hexadecylcyclohexane	42
5-Cyclohexayleicosane	66
OLEFINS	
1-Hexene	27
1-heptene	32
Vinyl cyclohexane	38
2,4,4-Trimethyl-1-pentene	10
2-Octene	43
1-Octene	41
2,6-Dimethylheptene	51
1-Nonene	51
1-Decene	56
1-Undecene	65
1-Dodecene	71
1-Tetradecene	80
2,6,7-Trimethyl-2,6-tridecadiene	24
2,2,6,6,8,8-Hexamethyl-4-methylene-nonane	5
1-Hexadecene	86
5-Butyl-4-dodecene	45
4-Butyl-4-dodecene	45
7-Butyltridodecene	36
3,12-Diethyl-3,11-tetradecadiene	26
1-Octadecene	90
8-Propyl-8-pentadecene	45
7,10-Dimethyl-8-hexadecene	43
9-Methyl-9-heptadecene	66
7-Hexyl-7-pentadecene	47
10,13-Dimethyl-11-doeicosene	56
4-Methyl-1-cyclohexene	28
4-Vinyl-1-cyclohexene	32
AROMATICS	
Benzene	0
Toluene	7
Ethyl benzene	8
1,4-Dimethylbenzene	−3
1,3-Dimethylbenzene	1
1,2-Dimethylbenzene	8
Isopropyl benzene	15
ter-Butyl benzene	−1
1,2,3,4-Tetramethylbenzene	17
Sec-Butylbenzene	6
1,3-Diethylbenzene	9
1-Methyl-4-isopropylbenzene	2
n-Pentylbenzene	13
Biphenyl	21
m-Diisopropylbenzene	−7
n-Hexylbenzene	26
Diphenylmethane	11
n-Propyltetralin	8
n-Heptylbenzene	35
1,2-Diphenylethane	1
tert-Butyltetralin	17
Sec-Butyltetralin	7
n-Butyltetralin	16
n-Octylbenzene	32
2-Phenyloctane	33
n-Nonylbenzene	50
n-Octylxylene	20
2-Phenyl-2-undecene	23
2-Phenylundecane	51
n-Octyltetralin	18
4-Phenyldodecene	42
n-Dodecylbenzene	68
7-Phenyltridecane	41
2-Phenyltetradecane	49
n-Tetradecylbenzene	72
2-Methyl-2-phenylpentadecane	39
2-Methyl-4-isobutyl-4-phenylundecane	18
2-Methyl-2-phenylheptadecane	39
1,2,4-Trimethyl-5-hexadecylbenzene	42
di-*n*-Octyltetralin	26
5-Phenyleicosane	39
Tetralin	13
1-Methylnaphthalene	0
2,6-Dimethylnaphthalene	−13
2-(1,1-dimethylethyl)-naphthalene	3
1-*n*-butylnaphthalene	6
2-Methyl-2-(beta-naphthyl)hexane	10
2-Octylnaphthalene	18
4-Methyl-4-(2-naphthyl)heptane	9
3,6-Dimethyl-3-(beta-naphthyl)octane	18
5-Methyl-5-(beta-naphthyl)nonane	12
2-Methyl-2-(beta-naphthyl)decane	18
3-Ethyl-3-(beta-naphthyl)nonane	13

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