

Aromatic Saturation: A Means to Cleaner Transportation Fuels

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Abstract

In the era of highly informed public opinions about environmental issues, requirement of "reformulated" transportation fuels need not be over-emphasized. In this work recent developments pertaining to compositional changes of diesel, chiefly saturation of aromatics, including those with multi-rings, have been reviewed. High aromatic content results in low cetane number of diesel and increased emission of particulate matters. These particulate matters as well as aromatics are known to be responsible for diseases like cancer, tuberculosis, etc. Here reactivity of aromatic compounds in hydrogenation reaction, thermodynamic, catalysis, and kinetic aspects of hydrodearomatization reaction have been addressed. . Effects of poison like sulfur on the catalysts' performance and methods to resist the poisons have been discussed.

Introduction

In recent years, awareness of even common people towards the health risks (e.g. carcinogenicity and particulate emissions) attached with the aromatic content of fuels, especially gasoline and diesel, has increased appreciably. Technically, the aromatics impart poor ignition quality and low cetane number of diesel and enhance smoke point of jet fuel. The particulates emitted by automobiles are responsible for diseases like cancer, tuberculosis, etc. For these reasons aromatic saturation has been drawing attention of the researchers the world over. With an increased use of FCC in the United States, more LCO was added to the diesel pool which resulted in enhanced aromatic content of diesel accompanied by a drop in Cetane number from 50 to 45 during the

period of 1960 to 1986 as shown in Table 1[1].

Table 1. Diesel fuel quality in United States

Year	Cetane number
1960	50
1965	49.5
1970	49
1975	48.5
1980	46
1985	45

However, due to evidence of carcinogenicity of aromatics, legislation were introduced in Sweden in 1991 (Table 2) and in California in 1993 (Table 3) limiting the aromatic content of diesel [2]. The Indian and European Diesel fuel specifications respectively, are described in Tables 4 [3] and 5 [4].

Table 2. Diesel fuel specifications of Sweden

Property	Urban Diesel- I	Urban Diesel- II	Standard Winter II
Sulfur Content (wt % max)	0.001	0.005	0.20
Aromatics (vol % max)	25	15	-
Density (Kg/m ³)	800-820	800-820	800-840
Cetane Number (minimum)	50	47	48

Table 3. Diesel fuel specifications of California

Property	Limit
Sulfur Content (wt % max)	0.05
Aromatics (vol % max)	10
Density (Kg/m ³)	830- 860
Cetane Number (minimum)	48

Table 4. Diesel fuel specifications of India

Property	Limit
Sulfur Content (wt % max)	0.5
Density (kg/m ³)	820- 845 (from 2005)
Cetane Number (min)	48 (to 51 in 2005)

Table 5. Diesel fuel specifications of Europe

Diesel fuel	1996	2000	2005	2005-2010
Sulfur Content (max)	500 ppm	350 ppm	50 ppm	10-30 ppm
Polyaromatics	Not specified	11 %	From 11 % to 2 %	1 % - 2 %
Density (Kg/m ³)	860	845	845 to 820	<840
Cetane Number (minimum)	49	51	From 51 to 58	53 up to 55

Presently conventional hydrotreating technology has been adapted for aromatic saturation and it has been recognized that aromatic hydrogenation (AH) is more difficult than hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) under conditions that are normally used for hydrotreating [5].

Production of cleaner and environment-friendly fuels necessitates various hydro-treatments including desulfurization and hydrodearomatization. Decreasing the aromatic content increases the cetane number of diesel. An aromatic reduction of 10 wt% cetane number increases by 3 to 3.5 [6].

Hydrogenation process is normally carried out in a trickle bed reactor at an elevated temperature and hydrogen pressure. In the common set up the liquid phase flows

downwards through the reactor concurrently with gas phase that partly consists of vaporized compounds. The temperature and pressure ranges for the hydrogenation of aromatic hydrocarbons in a liquid phase batch reactor were reported to be 450-700 K and 3.5 –17 Mpa [7-9].

Aromatic compounds in petroleum distillate

The aromatics found in petroleum and the middle distillates are divided into four groups: 1.Monoaromatics, 2.Diaromatics; 3.Triaromatics; 4.Polycyclic aromatics Fused multiring aromatics compounds are hydrogenated more easily to the corresponding monoaromatics under mild hydrotreating conditions. The amount and type of aromatics in middle distillates show large variations depending on the origin of the feed. (Table 6) [2].

Table 6 Distribution of Aromatic Compounds

Aromatics (Vol %)	Mono-	Di-	Tri-	Total
Heavy FCC Gasoline	38.8	5.5	0.5	44.8
Heavy Atmos. Gas oil	22.5	8.5	0.7	31.7
Light Coker Gas oil	16.3	16.4	8.0	40.7
Light Atmos. Gas oil	16.5	7.0	0.1	23.6
Light Cycle Oil	8.2	69.8	4.0	82.0
Straight Run Kerosene	15.7	1.7	0.1	17.5

Reactivity of Aromatic Compounds in Hydrogenation Reaction

On all catalysts, the rate of hydrodearomatization generally increases with the number of aromatic rings present, i.e. a low rate of hydrogenation is observed for monoaromatic ring such as benzene. The greater reactivity for hydrodearomatization with highest fused ring systems such as naphthalene and anthracene, is due to the fact that the resonance energy of the second ring of these multiple compounds is less than that for benzene [10]. The reactions of hydrogenation is favored by highly electron-donating substituents. Hydrogenation is easier when the ring to be hydrogenated is less aromatic [11]. The partial resonance energy or aromaticity of the different rings in fused multiring aromatic systems may be different. In multiring aromatic species, the ring with the lowest aromaticity is hydrogenated first. The following order of reactivity for one ring hydrogenation: Anthracene > Naphthalene > Phenanthrene > Benzene. Effects of various factors influencing the hydrogenation reactivity of aromatics and hydrocarbons have been reported by Sanati et al [5].

Thermodynamics

The hydrodearomatization reaction is reversible and at normal hydrotreating conditions, the complete conversion is not possible because of equilibrium limitations. The hydrogenation of an aromatic species, A is given by,

$A + nH_2 \rightarrow AH$, where AH is the hydrogenated product.

The equilibrium concentration of an aromatic compound is given [12] by,

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

where, Y_A = Mole fractions of the aromatic;
 Y_{AH} = Mole fractions of the hydrogenated aromatic (i.e., naphthene); K_a = Equilibrium-constant; P_{H_2} = Partial pressure of

hydrogen; n = Number of moles of hydrogen required for saturation

Above equation indicates that high pressures favour low equilibrium concentration of aromatics. Aromatic hydrogenation reactions are exothermic with heats of reaction between 63 and 71 kJ/mol H_2 [13,14]. K_a decreases and equilibrium aromatics concentration increases with temperature.

In benzene homologous hydrogenation, the value of the equilibrium constant decreases with and increases in both the number of side chains and the number of carbon atoms in each side chain [15, 16]. For more than one ring, hydrogenation proceeds via successive steps, each of which is reversible. The equilibrium constant is generally higher for the hydrogenation of the first ring [15], but more moles of hydrogen are involved in the final ring hydrogenation reaction. Usually hydrogenation of the first ring is thermodynamically less favored than that of the final ring at typical hydrotreating conditions.

Kinetics

Some authors [17-19] have shown that the aromatic content of the product decreases upto certain temperature and then increases, i.e., the aromatic content passes through a minimum. Thus, at lower temperatures, the reaction is kinetically controlled, while at higher temperatures, equilibrium controlled.

The kinetic data showed that all reactions were first order in hydrogen and zero order in aromatic compound concentration, indicating a near saturation coverage of the active sites by aromatic species [20]. A use of highly acidic oxide supports (e.g., $SiO_2-Al_2O_3$, TiO_2) was found to markedly enhance the hydrogenation rate.

Catalysts

Aromatic hydrogenation in industrial feed stocks may be carried out over supported metal or metal sulfide catalysts depending on the sulfur and nitrogen levels in the

feedstock. The choice of catalyst varies with applications, nature of the feedstocks and desired activity/selectivity of the reactions. This is briefly described below.

(1) Metal sulfides: Among the conventional catalysts, CoMo, NiMo or NiW on alumina are used for aromatic saturation. Maximum hydrogenation activity has been obtained with Ni-based catalysts with high metal loading, where the pore size distribution is selected to give maximum activity and stability [2]. However, their use has remained limited due to their higher costs and low turnover frequencies afforded by them. Metal sulfide catalysts can only accomplish moderate levels of aromatic saturation under typical hydrotreating conditions. Because of thermodynamic limitations a deep level of aromatic saturation cannot be achieved by increasing operation severity [5].

(2) Noble metals: Supported noble metal catalysts are well known for their high hydrogenation activity at low reaction temperatures and moderate hydrogen pressures for deep hydrodearomatization and also for their low resistance to sulfur poisoning [21, 22].

In this category, three sub-types have been studied. (A) Mono-metallic catalyst can be used only in the absence of sulfur in the feed stocks; (B) Bimetallic catalysts, a combination of Pt, Pd, Rh, Ir or Re have been shown to exhibit a better resistance to sulfur; (C) A combination of the conventional hydrotreating catalysts promoted by a noble metal may contain three metals [5]. The catalyst activity for the hydrogenation of benzene was reported to be in order $Rh > Ru \gg Pt \gg Pd \gg Ni > Co$ [23].

High intrinsic activity and sulfur tolerance may be enhanced by deposition of noble metals on acidic, high surface area supports, e.g., a large-pore zeolites beta [24, 25] and HY [26-28]. It has been established that noble metals deposited on acidic supports

show higher turnover frequencies (TOF) than when they are supported on non-acidic carriers.

The activity, selectivity and resistance to poisoning of these catalysts depend to a large extent on the location, size/ dispersion and structure of the metal particles in zeolites, which in turn are strictly controlled by the preparation and pretreatment conditions.

The enhancement in the S- tolerance of noble metals when supported on acidic carriers has been related to modification of the electronic properties of the metal atom resulting from interaction with the Brønsted acid sites of the support (electron acceptor)[29-31] or a bi- (multi-) metallic interaction [24,32,33]. Both effects lead to the formation of electron deficient metal sites, which in turn lowers the strength of the S-M bond [24, 29-31].

Conclusion

Catalyst development or improvement is going to play a pivotal role in the drive for producing high quality enviro-friendly fuels. Recent developments of sulfur tolerant catalysts afford a high degree of aromatic saturation can be achieved at moderate pressure. At present the market is almost exclusively confined to units supplying low aromatic diesel to the Swedish and the Californian markets. The question is to what an extent new legislation and new applications will result in an expansion of the new market. New legislations will include a requirement for higher cetane number. A high estimate might be a minimum cetane number of 50 in the US and 55 in the EU. A minimum cetane number of 50 in the US would be equivalent to an aromatic content of about 20vol% against the present 35vol%, requiring a considerable new capacity for hydrogenation. New materials, especially, zeolites are going to play a major role in this development.

References

- [1] G. H. Unzelman, AM-87-33, NPRA Annual Meeting, March 1987.
- [2] B. H. Cooper and B. B. L. Donnis, Appl. Catal. A: General 137(1996)203.
- [3] Central Pollution Control Board of India website.
- [4] P. Courty and J. F. Gruson, Oil and Gas Science and Technology - Rev. IFP, 56(5)(2001)515.
- [5] M. Sanati, B. Harrysson, M. Faghihi, B. Gevert and S. Jaras, in Catalysis, Vol. 16, Royal Society of Chemistry, Cambridge, 2002, p.1.
- [6] R. P. Verma, A. C. Pulikottil, U. Manna and M. Santra, Bull. Catal. Soc.India, 1(2002)9.
- [7] A. V. Spare and B. C. Gates, Ind. Eng. Chem. Proc. Des. Dev., 20(1981)68.
- [8] S. C. Korr, M. T. Klein and R. J. Quann, Ind. Eng. Chem. Res., 34(1995)101.
- [9] J. J. Llano R. Rosal, H. Sastre and F. V. Diez, J. Chem. Technol. Biotechnol., 72(1998)74.
- [10] C. Moreau and P. Geneste, Factor affecting the reactivity of organic model compounds in Hydrotreating Reactions: Theoretical Aspects of Heterogeneous Catalysts, ed. J. Moffat, van Nostrand Reinhold, New York, 1990, p. 256-306.
- [11] C. Moreau, C. Aubert, R. Durand, N. Zmimita and P. Geneste, Catal. Today, 4(1988)117.
- [12] A. J. Gully and W. P. Balard, in Advances in Petroleum Chemistry and Refining Vol. 7 (J. J. Mcketta, Jr., ed.), Interscience Publishers, London, 1963, p. 241.
- [13] R. C. Reid, J. M. Pruasnitz and T. K. Sharewood, The Properties of Gases and Liquids, McGraw Hill, New York, 1977.
- [14] S. B. Jaffe, Ind. Eng. Chem. Proc.Des. Dev., 13(1974)34.
- [15] L. F. Lepage, Applied Heterogeneous Catalysis, Technip, Paris, 1987.
- [16] M. F. Wilson, I. P. Fisher and J. F. Kriz, Energy & Fuels, 1(1987)540.
- [17] M. F. Wilson, I. P. Fisher and J. F. Kriz, J. Catal., 95(1985)155.
- [18] D. C. McCulloch, Oil Gas J., 73 (1975) 53.
- [19] G. Matarresse, E. Santoro, R. Covini and F. Pignataro, Oil Gas J., 81(1983)111.
- [20] A. Stanislaus and B. H. Cooper, Catal. Rev. Sci. Eng., 36(1)(1994)75.
- [21] C. H. Bartholomew, P. K. Agrawal, J. R. Katzer, Adv. Catal., 31(1982)135.
- [22] J. Barbier, E. Lamy- Pitara, P. Marecot, J. P. Boitiaux, J. Cosyns and F. Verna, Adv. Catal., 37(1990) 279.
- [23] H. Greenfiel and N. Y. Ann, Acad. Sci., 214(1973)233.
- [24] J. K. Lee, H. K. Rhee, J. Catal., 177(1998)208.
- [25] S. G. Kukes, F. T. Clark and D. Hopkins, WIPO Patent WO 94/19429 (1994).
- [26] D. Hamilton, US Patent 4,640,764 (1987)
- [27] P. J. Angevine and S. M. Clark, US Patent 4,683,214 (1987)
- [28] J. K. Minderhoud and J. P. Lucien, European Patent 303,332 (1988)
- [29] S. T. Homeyer and W.M. H. Schatler, J. Catal., 117(1989)91.
- [30] W.M. H. Schatler and A. Yu. Stakheev, Catal. Today 12(1992)283.
- [31] S. T. Homeyer and W.M. H. Schatler, Stud. Surf. Sci. Catal., 49(1989)975.
- [32] R. M. Navarro, B. Pawelec, J. M. Trejo, R. Mariscal and J. L. G. Fierro, J. Catal., 189(2000)184.
- [33] T. Rades, M. Polisset- Thfoin and J. Fraissard, Topics in Catal., 11-12(2000)283.