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Hydro-thermal cracking of heavy oils and its model compound

Ming-Gang Yang[1,*], Ikusei Nakamura, Kaoru Fujimoto

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract

Liquid-phase cracking of vacuum gas oil (VGO) was performed over NiMo supported nonacidic catalysts under 713 K and 8.0 MPa of hydrogen in a batch reactor, which is termed hydro-thermal cracking. Compared with VGO thermal cracking under the same reaction conditions the new process showed the suppressed naphtha yield (from 22.4 to 13.5 wt.%) and VGO conversion (from 65.7 to 64.0 wt.%) and increased the middle distillate yield (from 44.3 to 49.3 wt.%). At the same conversion level, the yield ratio of middle distillates to naphtha for this new process was two times higher than that for VGO hydrocracking. The VGO hydrocracking over USY-supported NiMo proceeded at much lower temperatures but gave higher naphtha yields. Both the thermal cracking and the hydro-thermal cracking of *n*-dodecyl benzene ($C_6H_5(CH_2)_{11}CH_3$) yielded toluene as the major aromatic product, whereas its hydrocracking over NiMo/USY yielded benzene as the major aromatic product. The reaction mechanism of this new process was assumed to consist of thermal cracking of hydrocarbon molecules via the free radical chain mechanism and the catalytic hydroquenching of free radicals.

1. Introduction

As conventional crude oils have become more expensive, interest in processing heavier feeds has increased. These heavier feeds have vacuum residue contents of 40% or more, which may require processing in order to find a market. On the other hand, the increasing demand for transport fuels especially diesel fuel and the reducing demand for heating fuels have been recognized as a long-term necessity. The conversion of heavy petroleum fraction into valuable liquid products has been one of the important objectives for upgrading heavy petroleum oils. At present this conversion is mainly achieved by thermal cracking, catalytic cracking and hydrocracking [1,2].

In thermal cracking process hydrocarbons with higher molecular weight in heavy oils can be transformed to lighter hydrocarbon products by thermolysis at a higher temperature, which is accompanied with the formation of coke. The development of thermal cracking process for producing middle distillates has been limited because large amounts of gas and naphtha with lower quality are produced due to overcracking. Catalytic cracking is different from thermal cracking because C–C bond cleavage of hydrocarbons in the former occurs on a solid acid catalyst. However, the absence of a high partial pressure of hydrogen in the catalytic cracking process not only makes possible the rapid build up of coke on the catalyst but also results in products containing a

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*Corressponding author. Tel.: +001 814 863 6169; e-mail: mxy11@psu.edu

[1] Present address: Fuel Science Program, The Pennsylvania State University, University Park, PA 16802, USA.

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significant amount of olefinic and aromatic compounds. This not only accounts for the high-octane rating of the catalytic cracking gasoline, but also for the poor quality of middle distillates obtained in the catalytic cracking. Hydrocracking process using a metal supported solid acid catalyst is considered to be a fine method for producing high-quality motor fuels. In the hydrocracking process, the use of higher partial pressures of hydrogen and relatively low temperatures decreases the rate of coke formation and favors the hydrogenation of olefins and aromatic compounds. However, for increasing the yields of middle distillates, the conventional dual functional catalyst still need to be improved [3]. In acid catalyzed hydrocracking process, it is necessary to remove the basic nitrogen compounds from the feedstock because they poison the acidic sites of the catalyst. In addition, in order to prevent the deactivation of the catalyst caused by the deposited coke or coke precursor, the process needs to be operated at high hydrogen pressures that causes a high hydrogen consumption and high construction cost of the reactor.

In our previous work we have claimed a new process concept called 'transfer hydrocracking'. In the transfer hydrocracking the hydrogen atoms liberated during the dehydrogenation of polyaromatic hydrocarbons on an active carbon catalyst can transfer to hydrogenate other hydrocarbon compounds in thermal cracking reaction of residual oils. Thus the production of paraffin-rich distillates and asphaltene-free residual oils can be achieved with small or no hydrogen consumption [4,5]. We have also demonstrated that thermal cracking of atmospheric residue in the presence of Ni supported β-Al_2O_3 catalyst and a certain hydrogen pressure can produce coke-free products [6].

The aim of the present work is to establish a method to produce a high-quality middle distillate from vacuum gas oil (VGO) by utilizing a combination of thermal cracking and catalytic hydrogenation. We call this new process as 'hydro-thermal cracking' because it differs from typical thermal cracking, catalytic cracking and hydrocracking. In the present study results from hydro-thermal cracking are compared with those from thermal cracking and hydrocracking. The mechanism of the new process has been studied by a model reaction of *n*-dodecyl benzene cracking.

2. Experimental

A feedstock used in the present work, vacuum gas oil (VGO), was derived from the Middle Eastern crude and has the following properties: specific gravity (15/4°C) of 0.9263, sulfur content of 2.45 wt.%, and total nitrogen content of 1100 ppm. Its fractional composition is given in Fig. 1. *n*-Dodecyl benzene (>98%) used as a model compound was commercially available. Three kinds of catalysts, nickel and molybdenum (NiMo) supported on β-Al_2O_3 (commercially available material of K_2O 11%, Al_2O_3 87%, CaO 2% and specific surface area of 3 m^2/g), a home made active carbon (prepared from Yallourn coal, specific surface area 620 m^2/g), and commercially available USY zeolite (SiO_2/Al_2O_3 ratio: 8.6) were prepared from the mixed aqueous solution of Ni $(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$ by the impregnation and calcination at 723 K for 3 h to give 6.0 wt.% NiO and 11.8 wt.% MoO_3, NiMo/γ-Al_2O_3 was a commercial catalyst (TK-771, produced by Haldor Topsϕe A/S H). All catalysts were sulfided with a gas mixture of H_2 and H_2S (4:1 mole ratio) at 673 K for 2 h before they were used for the reaction.

VGO reaction was operated in three different processes. One is hydro-thermal cracking in which three kinds of catalysts, NiMo/γ-Al_2O_3, NiMo/AC and NiMo/β-Al_2O_3 were used. The next one is hydrocracking over NiMo/USY catalyst and the third one is thermal cracking in the absence of catalysts. In

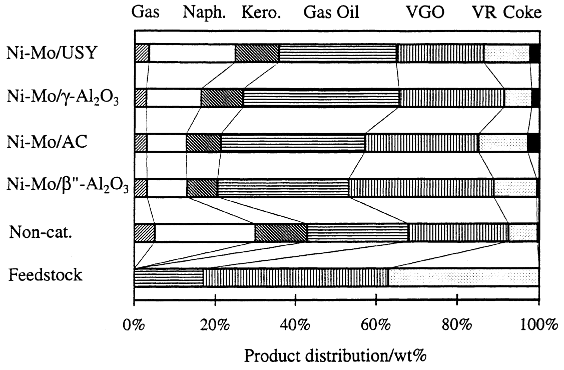


Fig. 1. Comparison of product distribution in VGO hydro-thermal cracking, hydrocracking, and thermal cracking. Reaction conditions: P: 8.0 MPa; VGO: 60 g; catalyst: 12 g; time: 60 min. T: 713 K except for NiMo/USY: 678 K.

every process the same hydrogen pressure was employed.

VGO cracking reactions were carried out in an autoclave with an inner volume of 150 ml. The reaction apparatus allows hydrogen gas to flow through the reactor during the reaction and to maintain constant reaction pressure. The typical reaction conditions for hydro-thermal cracking and thermal cracking were 713 K, 8.0 MPa and 60 min. In the NiMo/USY catalyst system, the reaction temperature was 678 K to obtain a comparable VGO conversion level to that of hydro-thermal cracking and to exclude the influence of thermal cracking. The model reaction of *n*-dodecyl benzene was carried out in a 75 ml batch autoclave, using the same catalyst under the conditions: 7.5 MPa, 60 min and 673 K for hydro-thermal cracking and thermal cracking but 593 K for hydrocracking.

Gaseous products generated in VGO cracking or in *n*-dodecyl benzene cracking were analyzed by FID gas chromatography provided with an active-alumina column. Fractional composition of the liquid products (naphtha, initial boiling point- 444 K; kerosene, 445–505 K; gas oil, 506–643 K; vacuum gas oil, 644–798 K and residue, >799 K) in VGO cracking was measured with a distillation gas chromatography provided with a silicone OV-1 glass column. The liquid products of *n*-dodecyl benzene cracking were clarified by GC-MS with OV-1 capillary column. The amount of coke was determined as toluene insoluble. Conversion of VGO cracking was calculated by the following formula

$$\text{Conversion(wt.\%)} = \left(1 - \frac{643\,\text{K}^{+}\ \text{fraction in product}}{643\text{K}^{+}\ \text{fraction in feedstock}}\right) \times 100$$

3. Results and discussion

One of the differences between hydro-thermal cracking and thermal cracking is the presence of NiMo-supported catalyst in the former. The hydro-thermal cracking is also different from the conventional hydrocracking which uses acidic dualfunctional catalysts.

3.1. Cracking of vacuum gas oil

Compared with the thermal cracking carried out under the same reaction conditions, the conversion level of VGO in the hydro-thermal cracking is lower as shown in Table 1 in which the conversion in the absence of catalyst was 65.7 wt.% whereas it was 64.0 wt.% for NiMo/γ-Al_2O_3, 52.6 for NiMo/AC, and 44.5 wt.% for NiMo/β-Al_2O_3 catalyst. The results indicate that the catalysts suppress the VGO cracking in the presence of gaseous hydrogen under thermal cracking conditions.

Table 1
Effects of various catalysts on gas composition in VGO cracking T: 713 K, P: 8.0 MPa, time: 60 min

Catalyst	Noncatalyst	Ni–Mo/β''-Al_2O_3	Ni–Mo/AC	Ni–Mo/γ-Al_2O_3	Ni–Mo/USY[a]
H_2 consumption/Nm^3/kl oil	2	49	78	51	102
Conversion/wt.%	65.7	44.5	52.6	64.0	61.6
Gas yield/wt.%	4.5	3.1	3.0	2.9	3.5
Gas selectivity/wt.%	6.3	5.8	5.0	4.3	5.2
Gas composition/wt.%					
C_1	23.7	16.1	23.5	22.8	4.3
C_2	27.8	19.6	23.8	24.8	8.6
C_2=	0.8	0.8	0.0	0.0	0.0
C_3	25.4	25.5	28.6	28.4	29.7
C_3=	3.6	4.5	0.1	0.1	0.2
i-C_4	3.3	5.2	5.7	5.2	28.6
n-C_4	8.9	12.8	11.2	11.5	14.3
C_4=	3.0	5.2	0.4	0.0	0.4
i-C_5	1.5	4.5	3.2	2.9	11.0
n-C_5	2.1	5.8	3.5	4.5	2.8

[a] 678 K.

Fig. 1 shows the product distribution of VGO cracking in the different reaction process. In the VGO thermal cracking, yields of naphtha and middle distillates (kerosene plus gas oil) are 22.4 and 44.3 wt.%, respectively. When NiMo/γ-Al_2O_3 is used as a catalyst under the same reaction conditions, the yield of naphtha is suppressed to 13.5 wt.% and that of middle distillates is increased to 49.3 wt.% with a small decrease in conversion. In the case of VGO hydrocracking on NiMo/USY catalyst, on the other hand, the yield of naphtha and middle distillates are 21.3 and 40.1 wt.%, respectively. Such effects of the NiMo-supported nonacidic catalysts (NiMo/γ-Al_2O_3, NiMo/AC or NiMo/β''-Al_2O_3) for increasing the yields of middle distillates are clearly shown in Fig. 2 in the ratio of middle distillates to naphtha, compared to the case of thermal cracking (noncatalyst) and hydrocracking (NiMo/USY). The ratio for VGO hydro-thermal cracking over NiMo/γ-Al_2O_3 is twice as large as that for the VGO hydrocracking or the VGO thermal cracking. It should be noted that although the product distribution for hydrocracking and thermal cracking processes is similar, the product quality is not the same. For example, the cetane number of gas oil from hydrocracking is 50, while that from thermal cracking is 41. In addition, while 97% of sulfur substances in VGO feedstock was removed in the former, only 12% was removed in the latter. In the hydro-thermal cracking, the cetane number of gas oil product is more than 50, and the desulfurization yield is more than 98%. This means that this new VGO cracking process can produce high quality middle distillates.

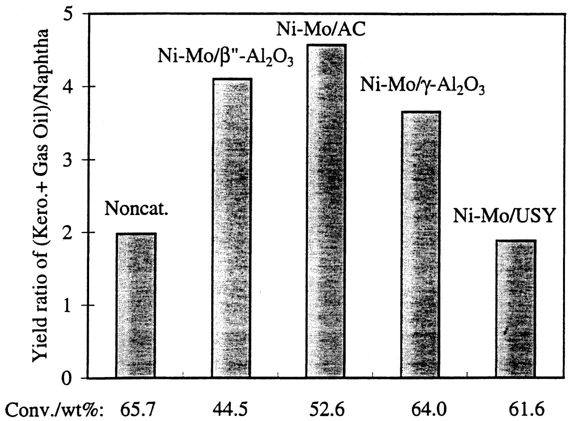


Fig. 2. Yield ratio of kerosene and gas oil to naphtha in VGO cracking in various catalyst systems. Reaction conditions: P: 8.0 MPa; VGO: 60 g; catalyst: 12 g; time: 60 min. T:713 K except for NiMo/USY: 678 K.

Hydrocarbon composition of gaseous products in various VGO cracking processes is also given in Table 1. In the case of the thermal cracking (without catalyst), C_2 hydrocarbons are the major products but methane is formed also, in large amount. In contrast, large amounts of C_4 hydrocarbons are formed in the hydrocracking on NiMo/USY catalyst. In addition, the ratio i-C_4/n-C_4 is only 0.39 in the thermal cracking of VGO, whereas in hydrocracking, it is 2.0. It is clear that the reaction of VGO in the thermal cracking and the hydrocracking proceeds via completely different mechanisms. As is well-known, in hydrocracking, the C–C bond cleavage on the acidic sites of USY zeolite proceeds by carbenium ion mechanism [7]. Carbenium ions are easily isomerized to stable tertiary-carbenium ions to form branched hydrocarbons. Hence, large amounts of branched C_4 products can be formed in this reaction process. In thermal cracking, however, as hydrocarbons are cracked via free radical mechanism [8], gaseous C_1 and C_2 are produced in large amounts. It is noted that in VGO cracking by hydro-thermal cracking process, gaseous C_1 and C_2 hydrocarbons are also the major products as shown in Table 1. Among the C_4 products, the ratio of i-C_4/n-C_4 for NiMo/γ-Al_2O_3, NiMo/AC and NiMo/β''-Al_2O_3 is 0.45, 0.50 and 0.41, respectively. Based on these results, it can be concluded that in the hydro-thermal cracking process, cracking reaction of the feedstock to lower boiling-point fraction proceeds by free radical mechanism, which is similar to thermal cracking but different from that of hydrocracking. However, hydro-thermal cracking process markedly decrease the yields of gaseous products compared with thermal cracking. This difference is due to the presence of NiMo-supported catalyst in the hydro-thermal cracking.

Three kinds of materials, β''-Al_2O_3, active carbon, and γ-Al_2O_3, used as carriers for VGO hydro-thermal cracking catalysts gave quite different characters in their nature.

From the olefin content in the gaseous product listed in Table 1, the order of hydrogenation activity under hydro-thermal cracking conditions are in the following order: NiMo/γ-$Al_2O_3$$\geq$NiMo/AC>NiMo/$\beta''$-

Al_2O_3. This can be attributed to the high surface area and proper pore distribution of NiMo/γ-Al_2O_3. The surface area of NiMo/β''-Al_2O_3 is too small to disperse metals on it well. On the other hand, the amount of deposited coke was smallest in the β''-Al_2O_3 catalyzed system. It is known that appreciate acidity of the support can promote the hydrogenation activity of NiMo or CoMo catalysts [9,10]. Considering the relative surface acidity, β''-Al_2O_3 is basic, active carbon is neutral, and γ-Al_2O_3 is relatively acidic. The adsorption of reactants on the active sites or on the support surface is involved in hydrogenation. A basic support has a tendency to obstruct the adsorption of coke precursors, which are molecules with high electron density, such as aromatics or olefins, so that the deposited coke on NiMo/β''-Al_2O_3 catalyst is very small. This is probably another reason why NiMo/β''-Al_2O_3 shows low activity for olefin hydrogenation. 49 Nm^3/kl-oil of hydrogen was consumed in the NiMo/β''-Al_2O_3 reaction system, however, NiMo/β''-Al_2O_3 catalyst showed low activity for olefin hydrogenation. We have already demonstrated that the concentration of free radicals in the hydro-thermal cracking of Kuwait atmospheric residue is controlled at a lower level in the presence of Ni/AC and pressurized hydrogen than in their absence. This result gave the conclusion that the catalyst can hydrogenate free radicals to stable molecules [11].

$$R^{\bullet} + 1/2H_2 \overset{\text{catalyst}}{\rightarrow} RH$$

Thus, it can be said that although, NiMo/γ-Al_2O_3 and NiMo/AC is able to hydrogenate both olefins and free radicals, NiMo/β''-Al_2O_3 can only be responsible for the hydrogenation of free radicals generated in the VGO thermal cracking by providing active hydrogen atoms. This effect results in the decrease in VGO conversion in thermal cracking because of the quenching of chain transfer. However, this hydrogen-quenching reaction produces another effect on product control, the higher middle distillate yield and lower gas and naphtha yield.

$$R^{\bullet} \rightarrow R'CH{=}CH_2 + R''^{\bullet}$$

$$R''^{\bullet} + RH(\text{feed}) \rightarrow R''H + R^{\bullet}$$

In the case of catalyzed reaction by NiMo/γ-Al_2O_3 or NiMO/AC, NiMo sulfides act as active sites not only for hydrogenating free radicals, but also for the hydrogenation of unsaturated hydrocarbons. In addition, due to its relative acidity of the support surface or due to the interaction of NiMo sulfides and the support, NiMo/γ-Al_2O_3 has also some cracking activity for hydrocarbons at high reaction temperatures. Hence, the VGO conversion on NiMo/γ-Al_2O_3 can be thought of as a result of such two effects. The effect of NiMo/AC catalyst lies between the effects of NiMo/γ-Al_2O_3 and NiMo/β''-Al_2O_3 catalysts.

It is well known that thermal cracking of hydrocarbon molecule proceeds via the chain reaction of free radicals that are generated by C–C bond cleavage or hydrogen atom abstraction. Therefore, if the free radicals are hydrogenated to stable molecules, the chain reaction is interrupted to reduce the reaction rate. The role of NiMo supported nonacidic catalyst are just to activate the hydrogen molecule to hydrogen atoms which can hydrogenate free radicals and olefins to suppress overcracking.

3.2. *Cracking of n-dodecyl benzene*

As is well known, alkylbenzene is cracked on a solid acid catalyst mainly to benzene and olefins via the promotion of α-carbon of alkyl benzene and its cracking, whereas in thermal cracking mainly to toluene and olefin through the fission of C–C bond dissociation [12,13]. Because of the marked difference in the product selectivity the cracking reaction of alkylbenzene can be used as a model reaction to distinguish a reaction whether, it proceed through by carbenium ion mechanism or free radical mechanism. In the present work, *n*-dodecyl benzene cracking is used as a model reaction to demonstrate the mechanism of the VGO hydro-thermal cracking process. In order to effect proper conversion in the model reaction and to prevent the model molecule from overcracking at relatively high reaction temperatures, the model reaction was carried out at temperatures lower than the corresponding VGO cracking.

The selectivities of major aromatic hydrocarbons (benzene and toluene) in *n*-dodecyl benzene cracking carried out in three types of reaction systems are shown in Fig. 3. Since the selectivity of aromatic hydrocarbon other than benzene and toluene was lesser that 10%, their selectivity can be the measure of the pattern of C–C bond dissociation of *n*-dodecyl benzene. When *n*-dodecyl benzene was cracked on the

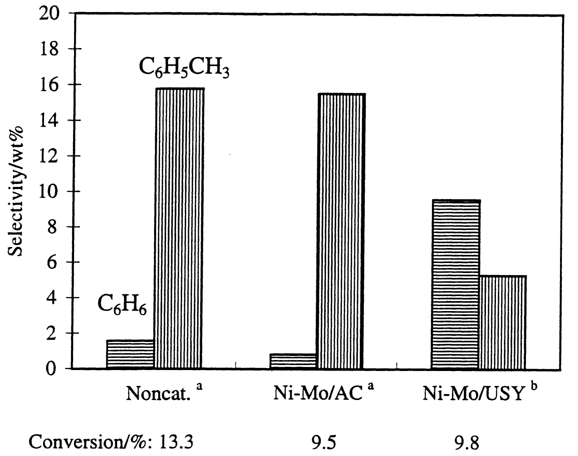


Fig. 3. Selectivity of benzene and toluene in aromatic hydrocarbons producedin C_6H_5 $(CH_2)_{11}CH_3$ cracking in different catalyst systems. Reaction conditions: P: 7.5 MPa; reactant: 20 g; catalyst: 1 g; Time: 60 min. T: (a) 673 K, (b) 593 K.

Table 2
Gas composition of C_6H_5 $(CH_2)_{11}CH_3$ cracking T: 673 K, P: 7.5 MPa, time: 60 min

Catalyst	Noncatalyst	Ni–Mo/AC	Ni–Mo/USY[a]
Conversion/wt.%	13.3	9.5	9.8
Composition/wt.%			
C_1	0.11	0.07	0.02
C_2	0.55	0.12	0.08
C_3	0.64	0.13	0.42
i-C_4	0.00	0.00	0.70
n-C_4	0.21	0.13	0.31
Selectivity/wt.%			
C_1	0.83	0.74	0.20
C_2	4.14	1.58	0.82
C_3	4.18	1.76	4.29
i-C_4	0.00	0.00	7.11
n-C_4	1.58	1.39	3.19
i-C_4/n-C_4	0	0	2.2

[a] 593K.

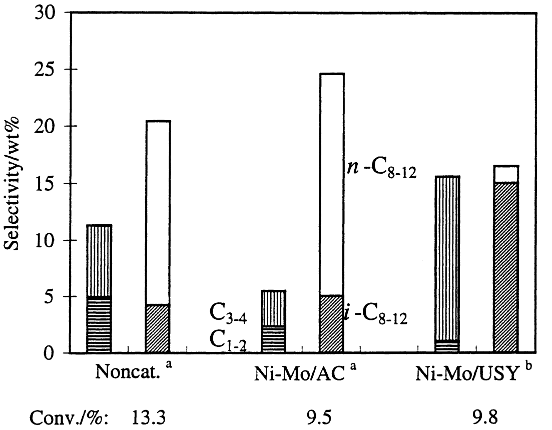
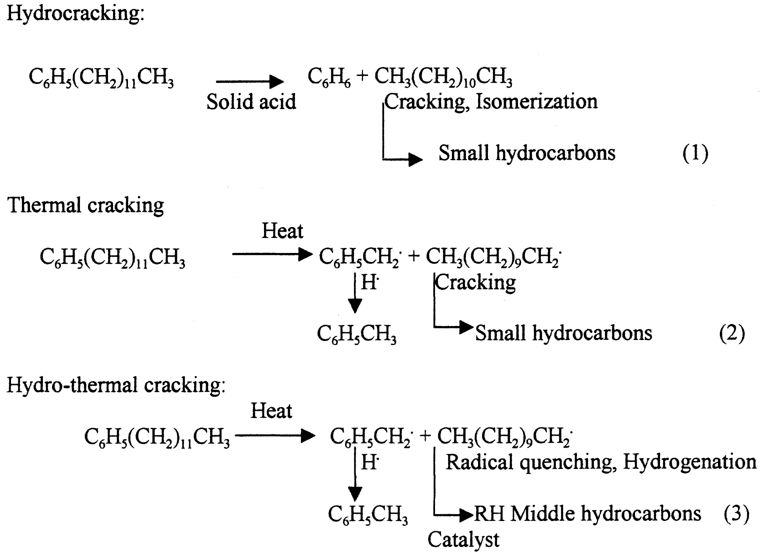


Fig. 4. Selectivity of $C_{1–2}$, $C_{3–4}$, i-$C_{8–12}$ and n-$C_{8–12}$ in C_6H_5 $(CH_2)_{11}CH_3$ cracking in different catalyst systems. Reaction conditions: P: 7.5 MPa; reactant: 20 g; catalyst: 1 g; time: 60 min; T: (a) 673 K, (b) 593 K.

NiMo/USY catalyst, the selectivity of the benzene product was higher than that of toluene, but when it was cracked thermally in the absence of any catalyst, the selectivity of toluene was much higher than that of the benzene product. When n-dodecyl benzene was cracked on NiMo/AC catalyst, the selectivity of toluene was also high. Hence, it is concluded that VGO cracking in hydro-thermal cracking process is carried out by free radical mechanism and is very different from that in hydrocracking process. This conclusion is also demonstrated by the composition of gaseous products in n-dodecyl benzene cracking in the three types of processes listed in Table 2. It shows a similar product distribution of gases to that of VGO cracking for the corresponding process listed in Table 1. In the thermal cracking and in the hydro-thermal cracking, C_1 and C_2 hydrocarbons among the gaseous products are high and C_4 products are mostly normal butane, whereas C_4 hydrocarbons are major gaseous products, in which the amount of i-butane is larger than that of n-butane.

It is also worthwhile to note the differences in paraffinic products resulted from the three types of processes. As shown in Fig. 4, when n-dodecyl benzene is cracked on NiMo/AC catalyst, the selectivity of alkane products from C_8 to C_{12} is very high, compared to that observed on NiMo/USY catalyst or in the case of noncatalyst. Among these $C_{8–12}$ products, normal hydrocarbons are major products on NiMo/AC catalyst, whereas on NiMo/USY catalyst, large amounts of isomerized nonaromatic hydrocarbon products are produced. This observation can be used to explain the difference in the selectivity resulted from hydro-thermal cracking and hydrocracking processes as clearly shown in Fig. 4, that in the hydro-thermal cracking process, the selectivity of $C_{8–12}$ products is higher while that of $C_{1–4}$ hydrocarbons is lower compared to the case of the hydrocracking process. Here, C_{8-12} hydrocarbons or their free radicals are produced in the first step of *n*-dodecyl benzene cracking, and they are further cracked to smaller hydrocarbon molecules, such as C_1–C_4 at high reaction temperatures. If NiMo catalyst exists in the thermal cracking process, it may activate gaseous hydrogen and hydrogenate C_{8-12} hydrocarbon radicals or olefins formed in the first step to suppress the secondary cracking of the radicals. Hence, these differences in product distribution are reasonably explained by the quenching of the hydrocarbon free radicals formed in the thermolysis by the catalytic action of NiMo/AC or NiMo/γ-Al_2O_3 catalyst and gaseous hydrogen. This reaction is shown in (equation (3)), which is different from hydrocracking (equation (1)) and thermal cracking (equation (2)).



4. Conclusions

A novel vacuum gas oil cracking process for increasing the middle distillate yield, which is called hydro-thermal cracking, is developed. Based on the results of the model reactions above, it can be concluded that in the hydro-thermal cracking process, hydrocarbon free radicals generated in thermolysis of VGO feedstock was hydrogenated by hydrogen atoms which are generated on hydrogenation catalysts NiMo/AC or NiMo/γ-Al_2O_3 or NiMo/β''-Al_2O_3 from gaseous hydrogen to form stable hydrocarbon molecules and consequently to suppress overcracking. This process can give an increased yield of middle distillates and suppress production of gas and naphtha.

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