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Hydrocracking and Hydroisomerization of Long-Chain *n*-Paraffins. Reactivity and Reaction Pathway for Base Oil Formation

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The formation of base oil components by the hydroconversion of long-chain *n*-paraffins [i.e., *n*-octacosane (*n*-C₂₈), *n*-hexatriacontane (*n*-C₃₆), and *n*-tetratetracontane (*n*-C₄₄)] on a 0.3% Pt/amorphous silica–alumina catalyst in a stirred microautoclave was investigated. The reaction pathway of hydroconversion, formation of base oil components, and kinetics were determined. The reaction can be described by a reaction network in which the conversion of *n*-paraffins occurs by three competitive reactions that directly lead to the formation of cracking products and two pseudocomponents: iso-C_{*n*} lube (i.e., lump of isoparaffins with sufficiently low pour points to make them suitable for a base oil) and iso-C_{*n*} nolube (i.e., lump of isoparaffins with pour points that are too high, making them unsuitable for a base oil). During reaction, the iso-C_{*n*} nolube fraction is converted into iso-C_{*n*} lube through subsequent hydroisomerization reactions. Both iso-C_{*n*} lube and iso-C_{*n*} nolube pseudocomponents further react to give cracking products. The conversion rate constants showed a significant decrease with increasing chain length, whereas the energies of activation did not display any significant change. A consistent decrease of iso-C_{*n*} and iso-C_{*n*} lube selectivity for longer chain lengths was observed, whereas reaction temperature was not found to play a significant role in determining the maximum yields of both iso-C_{*n*} and iso-C_{*n*} lube that could be achieved.

Introduction

Several economic, environmental, and technological factors have led to changes in performance requirements of automotive and industrial lubricants such as volatility, thermal and oxidation stability, and cold flow properties. Often, the more stringent specifications of these performances cannot be satisfied using traditional solvent refined mineral oil, so a shift toward “unconventional” aromatics-free base oils obtained via hydroprocessing is occurring. One of the reasons for the shift to saturate-rich products stems from the improved oxidation stability of these chemical structures compared to aromatic products.

Another reason for the use of these new unconventional base oils is their high viscosity index, which positively affects the reduction of volatility, leading to a decrease in oil consumption and providing an opportunity for improved fuel economy benefits.

Unconventional base oils can be produced by treating different feedstocks such as vacuum gasoil, deasphalted oil, slack waxes, or FT waxes.^{1,2} The higher quality of the base oils thus obtained derives from their different compositions, which contain lower contents, or even the absence, of aromatic compounds; lower concentrations of naphthenic structures; and conversely, higher percentages of isoparaffinic compounds respect with conventional base oil. The latter is the class of compounds with the best properties in terms of the viscosity index thermal stability and viscosity versus boiling point.³ Therefore, regardless of the feedstock, it is necessary that *n*-paraffins and possibly naphthenes be effectively converted into isoparaffins to produce low-pour-point

saturated products having good low-temperature fluidity, without significantly affecting the overall production yield. In this connection, the hydroisomerization reaction of aliphatic chains plays a fundamental role because it allows the melting points of paraffinic and naphthenic compounds to be greatly decreased while leaving unchanged their molecular weights. As an example of the changes caused by isomerization, note that the melting points of hexadecane, 5-methylpentadecane, 1-docosylcyclohexane, and 2-decyldodecylcyclohexane are 19, –31, 49, and –4 °C, respectively. Generally, the melting points of isoparaffins decrease with increasing degree of branching, but the size of the decrease depends on the position and length of the branching. Branching positions in the middle of the chain have a greater effect than those near the end of the chain, and longer side chains lead to a greater decreases of melting point.

The hydrocracking and hydroisomerization of long-chain paraffins over bifunctional catalysts have received increasing attention in the past two decades, and zeolites loaded with Pt and Pd have been widely used for this purpose.^{4–7} According to the bifunctional mechanism, the hydroisomerization and hydrocracking of normal paraffins occur through a series of consecutive reactions, where the cracking products are mainly formed through β -scission of di- and multibranched isoalkanes because these molecules can crack according to more energetically favorable β -scission modes not allowed for mono-branched and linear alkanes.⁸ The occurrence of consecutive reactions and the higher tendency of multibranched isoalkanes to crack explain why it is difficult to obtain high yields of multibranched isomers, which are the most desirable components of base oil because of their low melting points.

Hydroisomerization selectivity is affected by several factors (i.e., hydro/dehydrogenation activity of the metal, balance of metal-acid sites, porous structure and type

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of support).^{8–11} In the case of long-chain *n*-paraffins, high isomerization yields have been reported for a medium-pore zeolite (ZSM-22),⁷ a medium-pore silicoaluminophosphate (SAPO11),¹² and amorphous silica-alumina.^{13,14} In addition, high hydroisomerization selectivity has been obtained with another class of catalyst (molybdenum oxycarbide) that operates through a non-acidic mechanism.¹⁵ Whereas the hydroconversion of *n*-paraffins with chain lengths up to 16 carbon atoms has been extensively investigated, relatively little is reported in the literature about the behavior of longer aliphatic^{16,17} chains, which are more representative of the paraffinic fraction in feeds used in hydroconversion processes. In a previous study,¹⁴ the hydroisomerization vs hydrocracking selectivity was determined as a function of conversion for *n*-C₁₆, *n*-C₂₈, and *n*-C₃₆ on Pt/amorphous SiO₂–Al₂O₃. In the present paper, we report the results of a new set of experiments on *n*-C₂₈, *n*-C₃₆, and *n*-C₄₄, the aim of which was to elucidate the reaction network leading to the formation of base oil components. To this end, a suitable analytical procedure has been adapted. The analysis of the results led to the proposal of a reaction scheme for which the related kinetics have been estimated.

Experimental Section

Details of the catalyst, experimental setup, and procedures for hydroconversion tests and analysis of products have been described elsewhere.¹⁴ Briefly, the catalyst used throughout the experiments was platinum supported on amorphous mesoporous silica–alumina (MSA) extruded with γ -alumina. The synthesis of the MSA active phase and the preparation of the extrudate were carried out following the procedures reported in refs 18 and 19. The noble metal was loaded onto the extrudate, previously ground to <50 μ m, by impregnation with a H₂PtCl₆ solution according to ref 13. The platinum content was 0.3%, and the dispersion, measured by hydrogen chemisorption, was 96%.

The hydroconversion tests were carried out in batch mode using a stirred microautoclave (30 mL) providing good catalyst–reactant mixing and gas–liquid mass transfer. A detailed description of the system can be found in the literature.²⁰ For each run, the reactor was charged with the desired amount of catalyst, dried previously in an oven at 250 °C under vacuum overnight, and the *n*-paraffin. Subsequently, the reactor was purged, pressurized with H₂, and heated. The time required to reach the reaction temperature was 11 min. During the reaction, the temperature and the pressure were kept constant within ± 1 °C and ± 0.2 MPa, respectively. After the reaction, the reactor was cooled to room temperature and, following withdrawal of a sample of gas, depressurized. The gaseous products were analyzed on an HP-5890 II GC equipped with an MS detector through a 50-m HP-PONA column. The analysis of the liquid products was carried out on an HP-5890 II GC supplied with an on-column injection system using a 40-m HP-1 capillary column and a Fison 800 GC equipped with a 60-m-long capillary column (Supleco SPB-1). Because the consistency of the reaction products changed from solid to slurry depending on the degree of conversion, the sample for GC analysis was dissolved in CS₂. However, in this case, it was not possible to determine the concentrations of the cracking products lighter than C₇, which were evaluated through a second GC analysis with the sample dissolved in *n*-C₁₆.

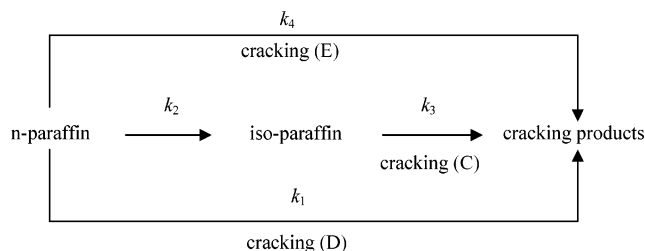


Figure 1. Reaction network for the hydroisomerization/hydrocracking of *n*-paraffins.¹⁴

The conversions of *n*-C₂₈, *n*-C₃₆, and *n*-C₄₄ were investigated at three temperatures (i.e., 345, 360, and 380 °C), with reaction times up to 32 h and a hydrogen pressure of 8.1 MPa. In each case, the ratio of catalyst (in grams) to *n*-paraffin (in moles) was 4.94.

Method for Determining the Base Oil Component of the Reaction Products. The base oil component of the reaction products is defined as the fraction with a boiling point higher than 365 °C that is soluble in a methyl ethyl ketone (MEK)/toluene (9:1) solution at –25 °C. The method used to determine the base oil content is described as follows: A known amount of reaction products (~100 mg) was placed in a 50-mL volumetric flask, diluted with a 90:10 solution of MEK/toluene, and heated to its complete miscibility (approximately 40–45 °C). The solution was then cooled at 1 °C/min to –25 °C and held at this temperature for 1 h. After that, an aliquot of the solution was withdrawn via a syringe supplied with a fritted steel filter (pore diameter = 2 μ m) on top of the needle and analyzed by gas chromatography. The determination of the base oil concentration was effected by injecting samples of the solution before and after cooling and measuring the overall areas of the peaks corresponding to compounds with chains longer than 22 carbon atoms (bp 369 °C).

Results and Discussion

Reaction Pathway and Kinetics of Base Oil Component Formation. For a given reaction, a general method that allows for the discrimination between the primary products (i.e., those formed directly from the reacting substrate) and those of a higher rank (i.e., those formed through consecutive reactions of intermediate products) is to plot the selectivity of the products (molar yield/conversion) against the conversion of the feed. The method, described in detail elsewhere,²¹ has general applicability, and it allows for the establishment of the ranks of the nonprimary products as well. This methodology has already been used to determine the reaction pathway of the hydroconversion of *n*-hexadecane⁹ and long-chain *n*-paraffins (*n*-C₁₆, *n*-C₂₈, and *n*-C₃₆)¹⁴ over platinum-loaded bifunctional catalysts. The results of the latter study indicated that, in the range of temperature 345–380 °C, hydrocracking and hydroisomerization of long-chain *n*-paraffins can be described by the reaction network shown in Figure 1, where the hydroconversion of the *n*-paraffins occurs through three competitive reactions [i.e., hydroisomerization (with rate constant k_2), catalytic hydrocracking (k_1), and thermal cracking or hydrocracking via radicals (k_4)]. In the present case, to determine the reaction network for the formation of base oil components, further hydroconversion tests were carried out, and the reaction products were subjected to solvent dewaxing tests, to determine

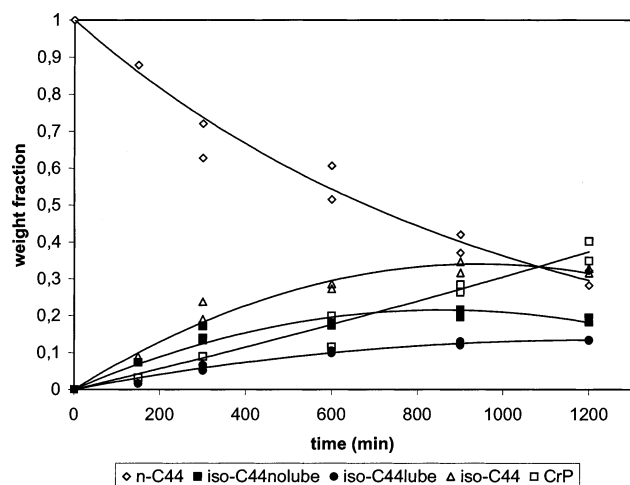


Figure 2. Changes in component concentrations as a function of reaction time. Concentration profiles predicted by the network shown in Figure 7 and experimental data at 360 °C.

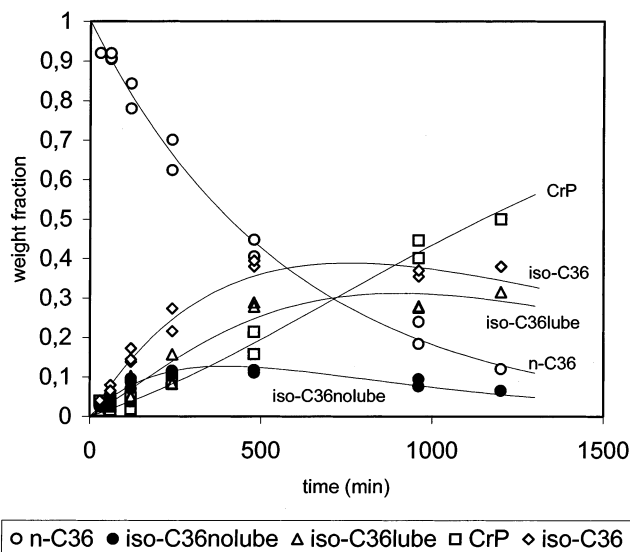


Figure 3. Changes in component concentrations as a function of reaction time. Concentration profiles predicted by the network shown in Figure 7 and experimental data at 360 °C.

the overall content of the compounds and the fraction of feed isomers soluble in MEK/toluene solution at -25 °C.

For clarity, the definitions of the pseudocomponents used in the present study are restated here: iso- C_n , isomer having the same number of carbon atoms as the reacted n -paraffin; iso- C_n lube, isomers of the feed that are soluble in MEK/toluene solution at -25 °C; iso- C_n nolube, isomers of the feed that are insoluble in MEK/toluene solution at -25 °C; and cracking products (CrP), normal and isoparaffins with at least one carbon atom less than the reacted n -paraffin.

As an example, Figures 2 and 3 show the yields of the various classes of feed isomers, as well as the n -paraffin and the cracking products, versus the reaction time. The patterns of evolution of the system are qualitatively similar at the three temperatures investigated (i.e., 345, 360, and 380 °C) and for all three n -paraffins. The concentration of the n -paraffin exponentially decreases, whereas the iso- C_n concentration initially increases, goes through a maximum, and thereafter decreases owing to the consecutive hydrocracking reaction. Similar trends are displayed by the

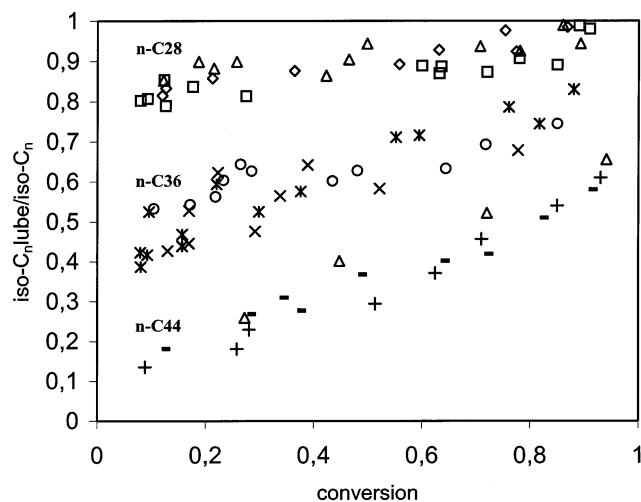


Figure 4. iso- C_n lube/iso- C_n ratio as a function of degree of conversion at the three temperatures investigated (345, 360, and 380 °C).

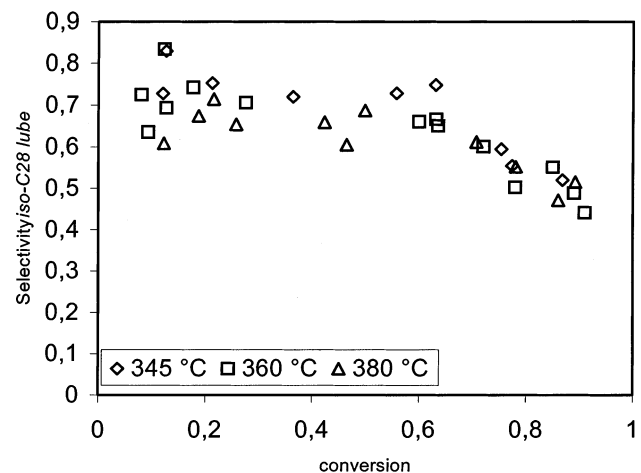


Figure 5. Conversion of n -C₂₈. First-order selectivity plot for the iso- C_n lube component of the reaction products.

iso- C_n lube and the iso- C_n nolube pseudocomponents of the isomers feed, although, as highlighted in Figure 4, a remarkable difference exists in terms of the relative concentrations of the iso- C_n lube and iso- C_n nolube pseudocomponents from n -C₂₈ to n -C₄₄. In each case (see Figures 5 and 6), when the selectivities for iso- C_n lube and iso- C_n nolube are plotted against the conversion of the n -paraffin, a positive intercept on the y axis is obtained for vanishing conversion. This result indicates that both the lube and nolube components of iso- C_n are directly formed from the n -paraffin. Furthermore, the decrease of the selectivity with increasing degree of conversion of the n -paraffin implies that both iso- C_n lube and iso- C_n nolube are intermediate products that further react. It has previously been shown¹⁴ that the selectivity for cracking products exhibits a positive intercept on the y axis at zero conversion, indicating that part of the cracking products are directly formed from the n -paraffin. Finally, the data obtained for n -C₄₄, where the trend is more evident (see Figure 7), show that the selectivity for iso-C₄₄ lube displays an initial increase, followed by a decrease at higher degrees of conversion. Whereas the decrease can be ascribed to the consecutive cracking reaction, the increase of selectivity for iso-C₄₄ lube at the lower bound of conversion can be rationalized assuming that the pseudocomponent iso-C₄₄ nolube further reacts to give iso-C₄₄ lube and

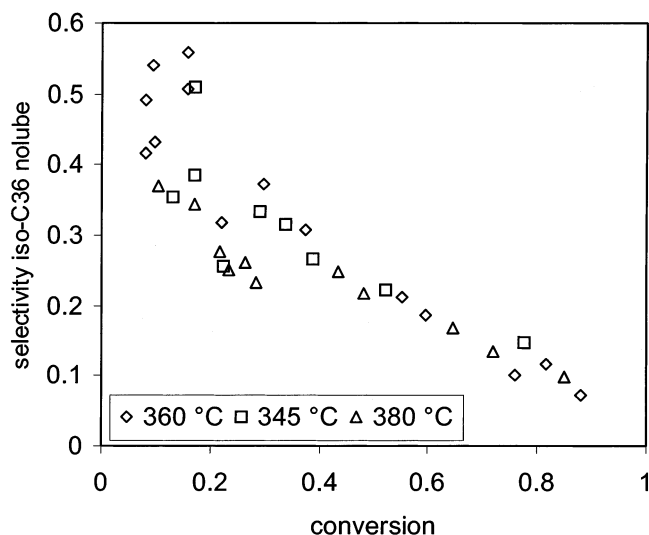


Figure 6. Conversion of $n\text{-C}_{36}$. First-order selectivity plot for the iso- C_n nolube component of the reaction products.

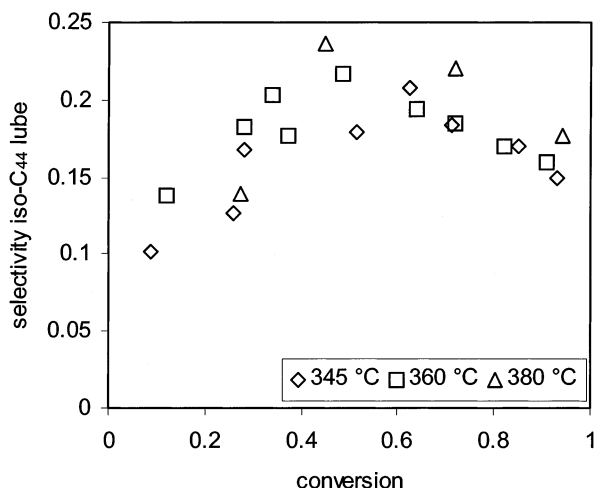


Figure 7. Conversion of $n\text{-C}_{44}$. First-order selectivity plot for the iso- C_n lube component of the reaction products.

cracking products. The presence of a reaction pathway that leads to the formation of iso- C_n lube from iso- C_n nolube is further supported by the data presented in Figure 4, which show an increase in the iso- C_n lube/iso- C_n ratio with increasing degree of conversion of the n -paraffin.

At any rate, the formation of iso- C_n lube compounds from iso- C_n nolube should merely be the consequence of the consecutive conversion of single-branched isomers into di- and tri-branched isomers, which have lower melting points. Considering the scheme presented in Figure 1 and the evidence presented so far, the conversion of n -paraffins into base oil components can be described by the reaction network shown in Figure 8. In this scheme, where the two reaction routes that lead to cracking products directly from the n -paraffin have been lumped together, the conversion of the n -paraffin occurs through three competitive reactions (with rate constants k_1 , k_2 , and k_3) which lead to the formation of iso- C_n lube, iso- C_n nolube, and cracking products, respectively; the former two further react (k_5 and k_6 , respectively) to yield cracking products. Moreover, during the reaction, the pseudocomponent iso- C_n nolube is converted into iso- C_n lube (k_4).

In this scheme, each single reaction was assumed to be irreversible and to follow pseudo-first-order kinetics.

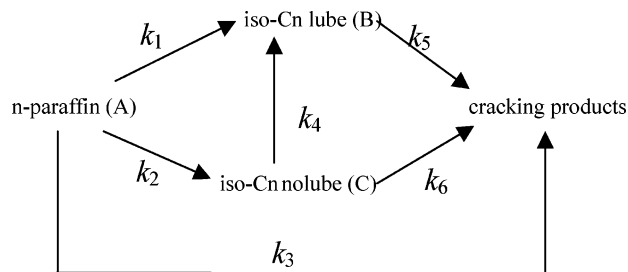


Figure 8. Reaction network for base oil component formation during the hydroisomerization/hydrocracking of n -paraffins (model 1).

The rate constants were determined by minimizing a merit function that contained the weighted sum of the square of the residual. The nonlinear regression analysis was carried out with a computer program (Scientist) that uses an extended version of Powell's algorithm for the minimization of the merit function. Initial parameter estimates were obtained as follows:

- (1) k_3 and $k_1 + k_2$ were known from a previous study.¹⁴
- (2) The data on the zero-conversion intercept of the plot of iso- C_n lube and iso- C_n nolube selectivity vs n -paraffin conversion gave the values of $k_1/(k_1 + k_2 + k_3)$ and $k_2/(k_1 + k_2 + k_3)$.
- (3) The values of k_4 , k_5 , and k_6 were estimated by nonlinear regression of the equations describing the evolution of the system, with k_1 , k_2 , and k_3 kept constant.

The values thus obtained were used for a preliminary estimate without weighting; then, on the basis of the preliminary results, the final regression was carried out using the appropriate values of weight factors. Because all of the parameters were unconstrained, nonlinear regression led in some cases to inconsistent results, mainly in terms of the variation of k_4 with the reaction temperature. Consequently, the following constraints were applied:

- (1) For each n -paraffin series, the value of the ratio $k_2/(k_1 + k_2)$ was kept constant and equal to the value of the iso- C_n lube/iso- C_n ratio at vanishing conversion at the three temperatures investigated (see Figure 4). Specifically, the value is 0.80 for $n\text{-C}_{28}$, 0.47 for $n\text{-C}_{36}$, and 0.23 for $n\text{-C}_{28}$. This constraint implies that k_1 and k_2 have the same energy of activation, E_{act} . Because both k_1 and k_2 refer to the isomerization reaction, this assumption can be considered reasonable.
- (2) For all of the n -paraffins and temperatures investigated, the following relationship was applied: $k_6 = yk_5$. The values of y that led to the best fitting of the experimental data was found to be 0.4.

The use of the last constraint is justified by the fact that the isomers with higher degrees of branching (iso- C_n lube) can crack more easily than the less-branched isomers of the iso- C_n nolube fraction.²² As an example, Figures 3 and 9 show comparisons between the experimental data and the predicted concentration profiles. The goodness of fit, evaluated in terms of the coefficient of determination, was always higher than 0.976.

Other models (see Table 1 and Figure 10) proved to be less significant. In this case, the significance of each model was evaluated by comparing the model selection criterion (MSC) values. The model selection criterion (MSC) is a modified version of the Akaike information criterion.²³ When comparing two models with different numbers of parameters, this criterion not only places a burden on the model with more parameters to have a

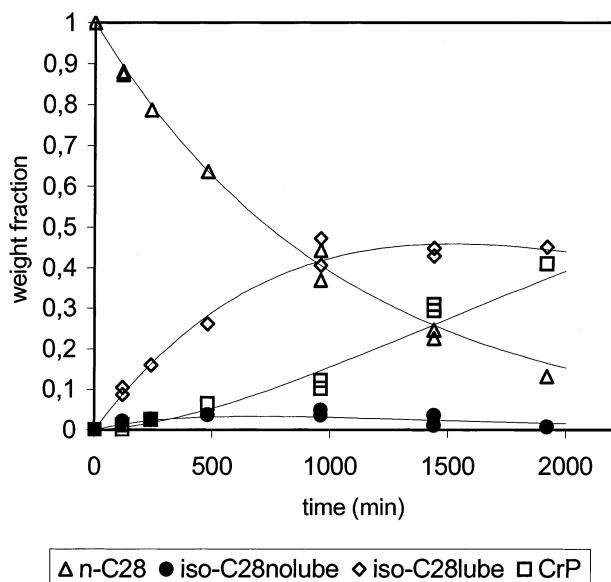


Figure 9. Changes in component concentrations as a function of reaction time. Concentration profiles predicted by the network shown in Figure 7 and experimental data at 345 °C.

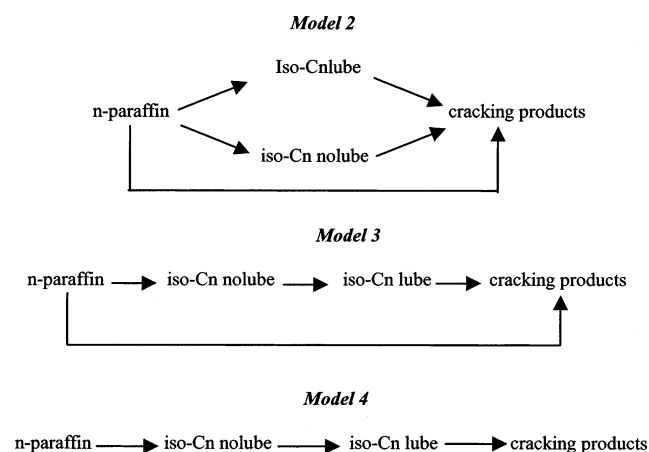


Figure 10. Alternative reaction network considered for the hydroconversion of *n*-paraffins.

Table 1. Model Selection Criterion (MSC) Values of Different Reaction Networks Examined

<i>n</i> -alkane	model 1	model 2	model 3	model 4
<i>n</i> -C ₂₈	5.52	4.65	3.29	3.57
<i>n</i> -C ₃₆	5.26	4.27	3.51	3.49
<i>n</i> -C ₄₄	4.96	3.92	3.57	3.14

Table 2. Activation Energies for the Observed Reaction Network

<i>n</i> -paraffin	E_{act} (kcal/mol)			
	k_1, k_2	k_3	k_4	k_5, k_6
<i>n</i> -C ₂₈	39 ± 3	63 ± 2	34 ± 3	35 ± 4
<i>n</i> -C ₃₆	36 ± 2	55 ± 4	34 ± 2	37 ± 3
<i>n</i> -C ₄₄	37 ± 4	58 ± 3	36 ± 4	39 ± 3

better coefficient of determination, but also quantifies how much better this coefficient must be for the model to be deemed more appropriate.

The estimates for the activation energies (see Table 2) give similar values for the hydroisomerization of *n*-paraffins to iso-*C_n* lube (k_1) and iso-*C_n* nolube (k_2) and their consecutive hydrocracking reactions (k_5, k_6), as well as the hydroisomerization of iso-*C_n* nolube to iso-*C_n* lube (k_4). In contrast, the E_{act} value related to the direct cracking of *n*-paraffins (k_3) is significantly higher.

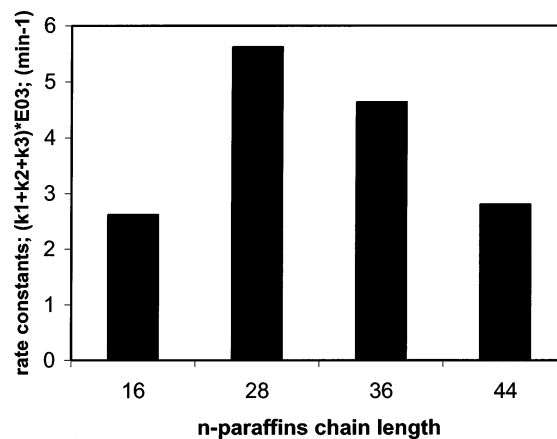


Figure 11. Effect of chain length on the overall conversion rate at 380 °C.

Such a difference can be explained in terms of the less energetically favorable pathway involved in the hydrocracking of *n*-paraffins respect with the isoparaffins.⁸ As for the energies of activation for the isomerization of *n*-paraffins and cracking of isoparaffins, the values found are similar to those reported by Steijns and Froment for the hydroconversion of *n*-decane and *n*-dodecane.²² These authors also found no significant difference between the E_{act} 's of hydroisomerization and hydrocracking. However, in a more recent paper²⁴ concerning the hydroconversion kinetics of *n*-C₈, *n*-C₁₀, *n*-C₁₁, *n*-C₁₂, *n*-C₁₃, and *n*-C₁₄, the values of E_{act} for hydroisomerization ranged between 38 and 43 kcal/mol, whereas the E_{act} values estimated were significantly lower, falling between 8.8 and 4.1 kcal/mol.

Several studies on the hydrocracking of *n*-paraffins up to 17 carbon atoms have clearly shown that their reactivity increases increasing chain length.^{6,24} Two possible causes might explain the dependence of reactivity on the chain length, namely (1) the higher number of secondary carbon atoms, as proposed by Sie,²⁵ and (2) the increase in the physisorption constant as a function of chain length.^{26,27}

The increase in reactivity was confirmed up to *n*-C₂₈ in our previous study,¹⁴ whereas a slight decrease was observed for *n*-C₃₆ with respect to *n*-C₂₈. Now, the decrease in reactivity for aliphatic chains longer than 28 carbon atoms is further confirmed by the new set of data referring to *n*-C₄₄. These findings are summarized in Figure 11. The observed decrease instead of the expected increase would suggest, at first sight, the presence of diffusion phenomena. However, even in the case of *n*-C₄₄, the energy of activation values reported in Table 2 do not seem to support this hypothesis. Tentatively, we suggest that the lower reactivities displayed by *n*-C₃₆ and *n*-C₄₄ might result from a decrease in the available surface area caused by the higher steric hindrance of *n*-C₃₆ and *n*-C₄₄ molecules.

A distinctive characteristic of the active phase of the catalyst is the sharp pore size distribution.¹⁸ It is possible, then, that a relatively small change in molecule size could result in a significant decrease in the amount of surface area accessible to the reactant. The data in Table 3 show that the average sizes²⁸ of the molecules used in this study are similar to the average pore diameter of the acidic phase.

Because *n*-paraffins can take up an enormous number of configurations through the rotation of chemical bonds, the average sizes of the *n*-paraffins were calculated by

Table 3. Lengths of End-to-End Vectors of *n*-Paraffins

<i>n</i> -paraffin	$\langle R \rangle$ (Å)
<i>n</i> -C ₂₈	11.2
<i>n</i> -C ₃₆	12.8
<i>n</i> -C ₄₄	14.2

Table 4. Maximum Yields of iso-C_{*n*} and iso-C_{*n*} lube

temp (°C)	iso-C ₂₈ (%)	iso-C ₂₈ lube (%)	iso-C ₃₆ (%)	iso-C ₃₆ lube (%)	iso-C ₄₄ (%)	iso-C ₄₄ lube (%)
380	46	43	32	23	29	14
360	49	46	39	30	30	13
345	47	45	35	26	28	15

a formula developed in the field of polymer dynamics, that is

$$\langle R^2 \rangle = Nb^2[(1 + \cos \theta)/(1 - \cos \theta)]$$

where *R* is the average length of the end-to-end vector of the molecule, *N* is the number of bonds, θ is the angle at which the *n*th bond is connected to the (*n* − 1)st bond, and *b* is the bond length.

Effect of Chain Length and Temperature on iso-C_{*n*} and iso-C_{*n*} Lube. The values reported in Table 4 point out that (1) the selectivity toward the formation of iso-C_{*n*} and iso-C_{*n*} lube displays a strong decrease as a function of the alkane molecular weight^{5,8,14} and the temperature does not have a significant effect on the maximum yields of both in iso-C_{*n*} and iso-C_{*n*} lube that can be achieved.

The effect of the temperature is consistent with the fact that, apart from *k*₃ whose values are the lowest anyway, the energies of activation of the other rate constants (i.e., *k*₁, *k*₂, *k*₄, *k*₅, and *k*₆) are very similar. Consequently, a change in the reaction temperature has the same effect on all of these rate constants.

As for the decrease of the selectivity for iso-C_{*n*} formation, a possible explanation has been suggested by Sie,²⁵ who proposed a difference in the dependence of the isomerization and cracking rate constants on chain length (i.e., C_n-6 for hydrocracking, C_n-4 for isomerization). The direct consequence of the different relationships is that the selectivity for isomerization decreases for longer *n*-paraffin chains. Another cause that can possibly explain the observed decrease is a change in the relative rates of desorption and β -scission of the iso-alkyl cations, which determine the overall selectivity toward isomerization.⁸

The data presented in Figure 4 indicate that the iso-C_{*n*} lube/iso-C_{*n*} ratio decreases markedly with increasing *n*-paraffin chain length.

In the case of *n*-C₂₈, most of the isoparaffins formed have a sufficient branching degree to make them soluble at −25 °C, whereas in the cases of *n*-C₃₆ and *n*-C₄₄, the fraction of iso-C_{*n*} lube is considerably lower. We suggest that the decrease of the iso-C_{*n*} lube/iso-C_{*n*} ratio for longer aliphatic chains is basically the result of two factors, that is, the different melting points of the *n*-paraffins (*n*-C₂₈, 64 °C; *n*-C₃₆, 75 °C; *n*-C₄₄, 88 °C) and the operating reaction pathway for the formation of the feed isomers. Studies on the hydrocracking/hydroisomerization of long-chain paraffins over bifunctional catalysts indicate that, with catalysts having a good balance between acidic and hydro/dehydrogenation functions, the reaction occurs through a series of consecutive reactions in which the *n*-paraffin is first isomerized into its monobranched isomers and subsequently into di- and tri-branched isomers. Assuming

that there are no differences in the isomerization process (i.e., type and position of side chains) related to the *n*-paraffin molecular weight, the drop of the melting point between the feed and the isomers depends on the branching degree, which, in turn, is proportional to the conversion. From this line of reasoning, it follows that the lower iso-C_{*n*} lube/iso-C_{*n*} ratio, at the same conversion level, observed for longer paraffins basically results from the higher gap between the melting point of the *n*-paraffin and the threshold value required to make the molecules soluble at −25 °C. In other words, the higher the melting point of the *n*-paraffin, the lower the fraction of isomers with a melting point below the threshold value *at a given degree of conversion*. The data at very low conversion levels (see Figure 4), where the iso-C_{*n*} lump is made up of single-branched isomers, indicate that the decrease of the melting point associated with the presence of one side chain per molecule makes 80% of the iso-C_{*n*} lump soluble in the case of C₂₈, whereas for C₃₆ and C₄₄, the percentages are 47 and 23%, respectively. In this connection, it is important to mention that previous results¹⁴ obtained with *n*-C₁₆ showed that, at very low conversion values, the isomers were almost exclusively single-branched and about 20% of them had an alkyl side chain longer than methyl. These data, together with the experimental evidence presented in this paper, indicate that the single-branched isomers formed in the first step, depending on the position and length of the side alkyl chain, give rise to the C_{*n*} lube and C_{*n*} nolube lumps. As previously reported, the melting point of isoparaffins decreases with increasing degree of branching, but the size of the decrease depends on the position and length of the branching. Branching positions in the middle of the chain have a greater effect than those near the end of the chain, whereas longer side chains lead to a greater decrease of the melting point. On this basis, it is conceivable that the higher the melting point of the *n*-paraffin, the lower fraction of single-branched isomers that present a suitable combination of length and position along the chain of the alkyl side chain to make them soluble at −25 °C. The C_{*n*} nolube lump, which does not have a sufficiently low melting point, is subsequently converted into the C_{*n*} lube lump through a consecutive isomerization reaction, which, in the reaction network presented in Figure 8, is the *k*₄ reaction.

Conclusions

The formation of base oil components during the hydroconversion of *n*-C₂₈, *n*-C₃₆, and *n*-C₄₄ over Pt/MSA catalyst was investigated. The experimental data evidenced that the hydroconversion of long-chain *n*-alkanes into corresponding base oil isoparaffins can be adequately described by a reaction network in which the conversion of the *n*-paraffins occurs by three competitive reactions that lead to the formation of cracking products, iso-C_{*n*} lube, and iso-C_{*n*} nolube. The latter two fractions are both intermediate products and further react to give cracking products. In addition, the presence of a reaction pathway that leads to the formation of iso-C_{*n*} lube components from the iso-C_{*n*} nolube fraction has been demonstrated. The selectivity for base oil components, and consequently the achievable maximum yield, decreases markedly with increasing aliphatic chain length. This result was shown to be the consequence of two factors: (1) First, the selectivity for hydroisomerization decreases for longer aliphatic chains. (2) Second, the

higher melting point of longer *n*-paraffins requires a higher branching degree, through consecutive isomerizations, to attain a sufficiently low melting point. However, because the hydroisomerization is always more or less extensively accompanied by hydrocracking, the overall process leads to lower yields of base oil components.

In contrast to what is generally reported in the literature for the hydrocracking of *n*-paraffins up to 17 carbons atoms, a decrease of reactivity was observed along the series *n*-C₂₈, *n*-C₃₆, *n*-C₄₄.

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