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Hydroconversion of Fischer–Tropsch waxes: Assessment of the operating conditions effect by factorial design experiments

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Abstract

The effect of operating conditions (temperature, space velocity, pressure and H_2/feed ratio) on the hydroconversion of Fischer–Tropsch wax and isomer content of the middle distillate was investigated by carrying out experiments according to a second order factorial design. The catalyst used was a 0.3% platinum/amorphous silica–alumina catalyst. Temperature and space velocity exhibited the biggest effect on wax conversion rate but a significant role was played by the pressure and the H_2/wax ratio as well. The results indicated an inverse relationship between pressure and conversion rate while an opposite behaviour was shown by the H_2/wax ratio. The effect of the last two variables was explained respectively in terms of the reaction mechanism of *n*-paraffins on bifuctional catalyst and the effect of the vapour–liquid equilibrium (VLE) on apparent conversion rate and isomer content of products.

Keywords: Hydroconversion; Fischer–Tropsch wax; H_2/wax ratio

1. Introduction

It is well known that the conversion of syngas through the Fischer–Tropsch (F–T) process leads to the formation of products essentially made up of *n*-paraffins (>90%), together with smaller percentages of alcohols and olefins. The F–T products are characterised by a wide range of molecular weights whose distribution can be described by the Anderson–Flory–Schulz model [1]. As consequence of the chain growth mechanism and the nature of the products, a large fraction of F–T products has a boiling point higher than 370 °C while the middle distillates (i.e. 150–370 °C cut) show very poor cold flow properties (i.e. relatively high melting point) that hamper their use as transportation fuel. A method adopted to overcome these limitations is to subject F–T products to a hydrocracking stage to improve both yields and quality of middle distillates [2,3]. During hydroconversion over a bifunctional catalyst the cracking of long chain alkanes leads to the increase of middle distillate fraction while isomerization remarkably improves their cold flow properties [4]. The hydrocracking catalysts are bifunctional catalysts, that is, they are characterized by the presence of two types of active sites: (1) the acid sites which provide the isomerization/cracking function; (2) the metal sites with hydrogenation–dehydrogenation function. Platinum, palladium or bimetallic systems (i.e. Ni/Mo, Ni/W, Co/Mo in the sulfided form) are the most commonly used metals. Catalysts loaded with a noble metal (particularly Pt) show better performances in terms of selectivity for hydroisomerization and products distribution [5–7] in comparison with non noble metals based catalyst. A distinctive characteristic of the products obtained via F–T synthesis and subsequent hydrocracking is the absence of heteroatoms (S and N) and aromatics. Recent studies indicated that emissions of hydrocarbons, CO, NO_x and particulates from F–T derived diesel are significantly lower than those from conventional diesel [8]. EniTecnologie is presently involved in a research program aimed at developing a gas to liquid technology to produce middle

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Table 1
Strength, amount and type (B: Brønsted, L: Lewis) of acid sites in the Pt/MSA/E sample

Acid strength							
Weak (µmol g^{-1}) 200 °C		Medium (µmol g^{-1}) 300 °C		Strong (µmol g^{-1}) 400 °C		Very strong (µmol g^{-1}) 500 °C	
L	B	L	B	L	B	L	B
210	21	131	9	71	9	41	0

distillates. Previous results showed that the quality of the products and their distribution are deeply affected by the operating conditions [9]. In the present paper we report the main results of a study where the effects of operating conditions on products distribution and quality have been investigated by factorial design experiments.

2. Experimental

The catalyst used throughout the experiments consisted of platinum supported on amorphous mesoporous silica–alumina (MSA), with a SiO_2/Al_2O_3 ratio of 100, extruded with a binder (γ-alumina). Details of the active phase synthesis and extrudate preparation are reported elsewhere [10–12].

The extrudate is characterized by a B.E.T. surface area of ~550 $m^2\,g^{-1}$, a bimodal pore size distribution as shown in Fig. 1 and the predominance of weak acid Brønsted sites (see Table 1). The MSA/γ-alumina weight ratio was 1.5. The noble metal was loaded on the extrudates through impregnation with a solution of H_2PtCl_6. The platinum content was 0.3%.

Hydrocracking tests were carried out in a bench scale trickle bed reactor operated in down flow mode. The reactor was charged with 9 g of catalyst previously crushed (average particle size: 0.6 mm). Gas and liquid products were analysed by gas chromatography. Hydrocracking products were lumped in the following cuts: $C_{1–4}$ (gas); $C_{5–9}$ (naphtha); $C_{10–14}$ (kerosene); $C_{15–22}$ (gasoil) and C_{22+}(atmospheric residue). The effect of operating conditions temperature, pressure, H_2/wax ratio and weight hourly space velocity (WHSV) was investigated by a second order factorial design, the so called central composite design (CCD) [13]. The ranges of the operating conditions were the following: temperature = 324–360 °C; pressure = 35–60 atm; H_2/wax = 0.06–0.15 wt/wt; WHSV = 1–3 h^{-1}. CCD consists of a complete 2^k factorial design with level coded to the −1, +1 level; Repeated center points (n_0) that in our case were 4; two axial point on the axis of each variable at distance α from the design center. In our case $\alpha = 2$ which makes the design rotatable that is the variance of predicted response Y′ remains constant at all points which are equidistant from the design center. Experiments carried out according to a factorial design allow to esteem in the most correct way the influence of the factors (i.e. temperature, WHSV, pressure and H_2/wax) on the response (i.e. conversion, isomer concentration, etc.) independently by the change of others factors and to evaluate the possible effect due to the interaction of variables. The analysis of the data by multivariate linear regression (MLR) allowed to determine the coefficients and their significance in the Eq. (1) which represents a complete p factors second order model

$$y = b_0 + \sum_{i=1,p} b_i x_i + \sum_{\substack{i=1,\,p-1\\ j=i+1,\,p}} b_{ij} x_i x_j + \sum_{i=1,p} b_i x_i^2 \qquad (1)$$

where y is the response, b the coefficients and x are the factors.

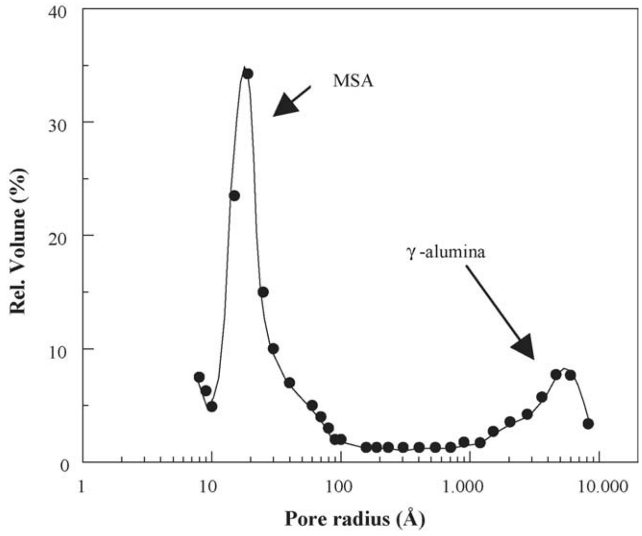

Fig. 1. Pore size distribution of the extruded catalyst.

Table 2
Composition of the feedstock

Cut	Weight fraction
C9−	0.037
C10–14	0.176
C15–22	0.301
C22+	0.486

Coded variables with levels −2, −1, 0, +1,+2 in place of the input variables were used.

The distribution among different cuts of the FT wax used in this study is given in Table 2

3. Results and discussion

As shown in Fig. 2 the yields of the middle distillate ($C_{10–22}$) increases up to 80–90% of C_{22+} conversion and thereafter decreases owing to greater presence of consecutive hydrocracking reactions which lead to lower molecular weight compounds such as $C_{5–9}$ fraction and gasses. The latter are almost exclusively made up of butane, isobutane and propane).

Table 3
Model for the conversion of the C_{22+} fraction

Coefficients	Value	Pr(>|t|)
Intercept	33.5071	<0.0000
Temperature	28.2873	<0.0000
Pressure	−4.8057	<0.0000
H_2/wax	3.3746	<0.0000
WHSV	−10.7304	<0.0000
Temperature^2	8.9877	<0.0000
$(H_2/wax)^2$	−1.8623	0.0042
WHSV^2	2.0946	0.0017
Temperature:H_2/wax	2.1744	0.0080
Temperature:WHSV	−5.4952	<0.0000

R^2: 0.9927, F: 231.3 on 9 and 18 degrees of freedom; p-value: 4.441e−016.

The results of MLR using as response the data of conversion of C_{22+} fraction – see Table 3 – indicates that all four factors considered (i.e. temperature, pressure, H_2/wax and WHSV) have a significant effect on C_{22+} conversion rate with the temperature and the WHSV playing the major role. Moreover, a significant effect on C_{22+} fraction conversion is due to the interaction temperature–H_2/wax and temperature–WHSV. With reference to the tables showing the models, the meaning of statistic values is given here below.

- p_{value}: gives the level for which the null hypothesis is accepted.
- R^2: the fraction of the total variance of the experimental data explained by the fitted model.
- F: $[SSR/(p-1)]/[SSE/(N-p)]$.
- Pr(>|t|): gives the probability that $b_i = 0$.

The conversion model is characterized both by an elevated R^2 value and high level of meaningfulness. The correspondence between experimental and estimated values is very good as illustrated in the parity plot shown in Fig. 3.

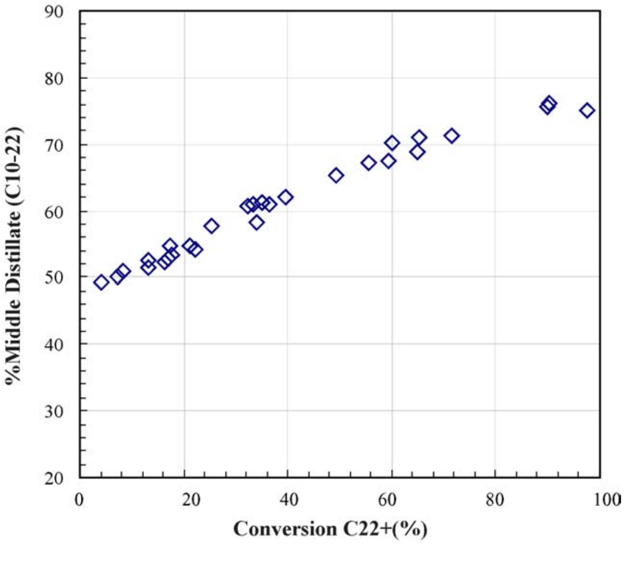

Fig. 2. Middle distillate yields vs. conversion of C_{22+} fraction.

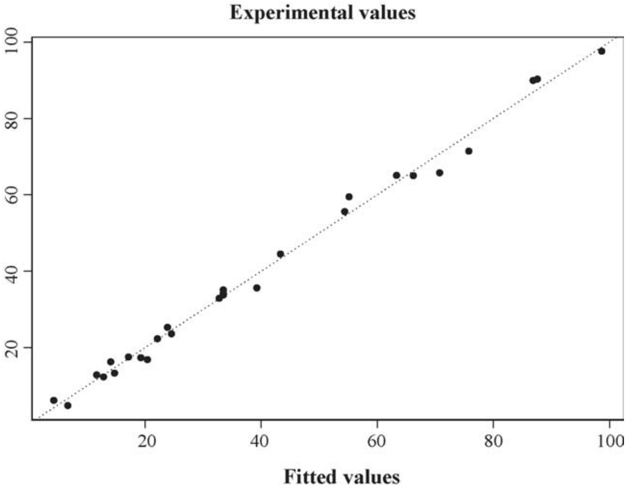

Fig. 3. Observed values vs. calculated for the percent conversion of C_{22+} fraction.

Besides the expected effect of temperature and WHSV, on the conversion degree of C_{22+} fraction, the negative sign of the pressure coefficient indicate that higher values of this factor leads to a decrease of C_{22+} conversion degree while the opposite happens as for the effect of H_2/wax ratio. The data reported in the Figs. 4 and 5 show graphically the effect of pressure and H_2/wax ration on conversion of C_{22+} fraction. Although the skeletal rearrangement and hydrocracking of n-paraffins occur without and with consumption of hydrogen, respectively, it is well known that rate constant for hydroisomerization/hydrocracking of n-paraffins is inversely proportional to the hydrogen pressure and the apparent reaction order with respect to hydrogen reported in literature are generally −1 [14] or slightly higher (−0.85) [15]. The negative dependence of C_{22+} conversion on hydrogen pressure can be explained in terms of bifunctional mechanism where the first step is the formation of olefins at the metal site, subsequently formation of secondary

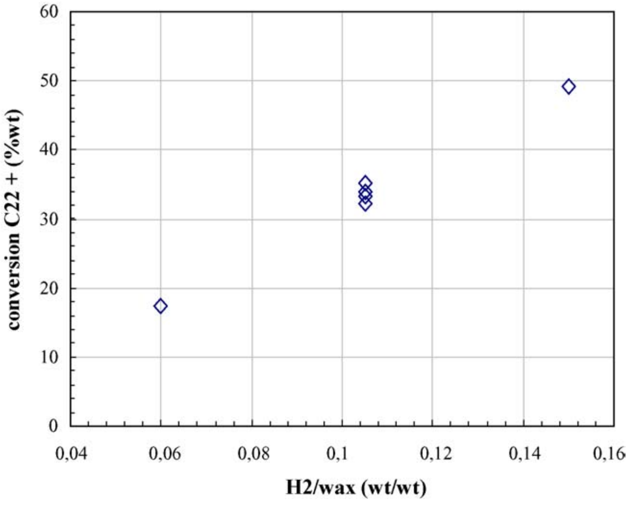

Fig. 4. Conversion of C_{22+} fraction as a function of H_2/wax ratio (pressure: 47.5 atm; H_2/wax: 0.105; WHSV: 2 h^{-1}).

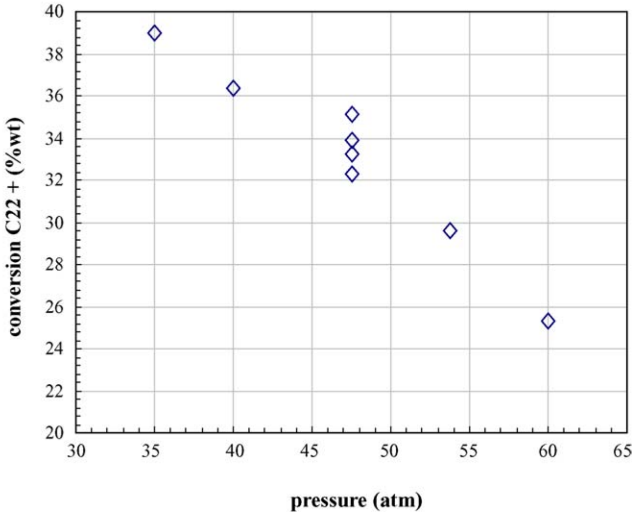

Fig. 5. Conversion of C_{22+} fraction as a function of total pressure (WHSV: 2 h^{-1}; temperature: 342 °C; H_2/wax: 0.105).

carbenium at the acidic site and then the various steps leading to the final products [14,16]. In this scheme the limiting step is the rearrangement of the secondary carbenium to tertiary carbenium while the other steps are considered to be at quasi equilibrium state. It is easy to see that in this case an increase of hydrogen pressure will lead to lower steady state concentrations of secondary carbenium ions with a consequent decrement of the limiting step rate.

The rate equations developed according to Langmuir–Hinshelwood formalism for isomerization (see Eq. (2)) and cracking reaction [17–19] point out that reaction rate increases with in increasing hydrocarbon partial pressure while opposite happens with the increase of hydrogen partial pressure. Furthermore, at constant total pressure higher H_2/hydrocarbon ratio in the reactor inlet would lead to a decrease of reaction rate [19] even in the case of strong physisorption of hydrocarbon [17,18].

$$R = k_{\text{iso}} \frac{K_{\text{dehydr}} K_{\text{prot}} (p_{n-p}/p_{H_2})}{1 + K_{\text{dehydr}} K_{\text{prot}} (p_{n-p}/p_{H_2})} \tag{2}$$

Differently to what foreseen by the Eq. (2) in our case an increase of H_2/wax ratio results in an increase of C_{22+} conversion rate.

Table 4
Effect of temperature and H_2/wax ratio on VLE (*H_2 free basis)

Pressure (atm)	35			
Temperature (°C)	324		360	
H_2/wax (w/w)	0.06	0.150	0.06	0.150
*V/F (feed) (w/w)	0.360	0.528	0.476	0.657
*Liquid phase composition (w/w)				
C_{10-14}	0.055	0. 026	0.035	0.015
C_{15-22}	0.264	0.202	0.207	0.119
C_{22+}	0.680	0.771	0.757	0.865

We suggest that the influence of the H_2/wax ratio is basically the result of the vapour–liquid equilibrium present in the reaction environment which, according to the operating conditions, leads to both different vapour/liquid ratios and phases composition. As previously shown [9,20] the vapour and liquid phase compositions, calculated by a routine based on SRK cubic equation of state, showed that the distribution of the feedstock and products between liquid and vapour phase as well as their compositions, was remarkably affected by the H_2/wax ratio. The data in Table 4 point out that higher H_2/wax ratios lead to a substantial increase of the vapour phase fraction and according to the operating conditions used the vapour/feed ratio (V/F) ranged from 0.36 to 0.66. Along with the increase of V/F ratio higher H_2/wax ratios lead to a heavier liquid phase containing a higher concentration of C_{22+} fraction. For the ideal trickle bed reactor where the catalyst particles are completely covered by the liquid and the reaction occurs only in the liquid phase in contact with the catalyst the reactant concentration C at the reactor outlet in presence of evaporation can be written as follows [21]:

$$C = C_0\, e^{-k/(1-\text{fs})\text{WHSV}} \tag{3}$$

where fs is the fraction of feed evaporated, C_0 is the reactant concentration in the feed while WHSV is the weight hourly space velocity. The Eq. (3) point out that in presence of evaporation the real WHSV of the liquid phase is lower than the overall one. Following this line of reasoning, the observed increase of C_{22+} fraction conversion at higher H_2/wax ratios is a consequence of the higher vaporization degrees (see Table 4) of feedstock which leads to lower space velocity of the liquid fraction in direct contact with the catalyst and consequently to higher conversions. Furthermore, the increase of C_{22+} fraction concentration in the liquid phase at higher H_2/wax ratios further enhances the phenomenon.

MLR considering as system response the isomer content of C_{10-14} and C_{15-22} fractions showed that the significant factors in this case were the temperature, pressure and

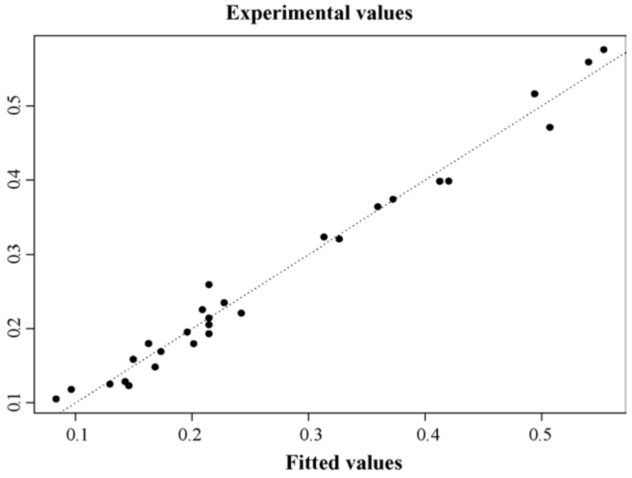

Fig. 6. Observed values vs. calculated for the isomer content of C_{10-14} fraction in the hydrocracking products.

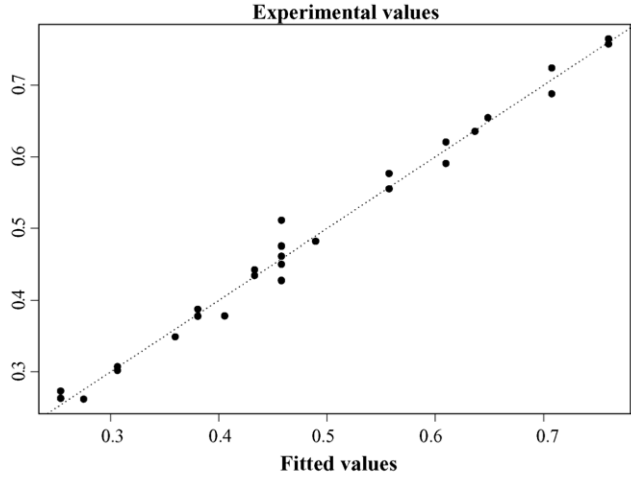

Fig. 7. Observed values vs. calculated for the isomer content of $C_{15–12}$ fraction in the hydrocracking products.

WHSV. The models obtained explained more than 98% of the variance of the experimental data and *F* values indicated a high degree meaningfulness. The correspondence between experimental and estimated values was very good as illustrated in the parity plot shown in Figs. 6 and 7.

The data in Tables 5 and 6 show that in both cases (i.e. $C_{10–14}$ and $C_{15–22}$) the temperature has a positive coefficient and plays the major effect. Differently, pressure and WHSV have an opposite effect that is higher value of these two factors lead to products with a lower isomer concentration. Apparently in contrast to what previously observed [9] the H_2/wax ratio does not seem to play any significant effect on the isomerization degree of the middle distillate fraction. Particularly, the data obtained at constant H_2/wax ratio, showed that at the same conversion level the isomer content of the middle distillate increased at lower H_2/wax ratios. The apparent discrepancy can be explained bearing in mind that lowering the H_2/wax ratio leads to a decrease of conversion of the C_{22+} fraction (see Fig. 2) which in turn results in a lower isomer content of products. Evidently, in our case there is a sort of compensation, between two phenomena having opposite effects on isomer content but both connected with H_2/wax ratio. As seen before one is the effect on conversion level while the other is the inverse relationship between degree of vaporization of the middle distillate fraction and the H_2/wax ratio. Previous results [9] showed that lower degrees of vaporization associated with lower H_2/wax ratios led to higher isomer content of middle distillate cut, when the comparison was made at the same conversion level. Therefore, we are in a situation of this type, lower H_2/wax ratios yield to lower conversion degrees but at the same time to an increase of isomer content so the net result is lower conversion but with the same isomer content of the products obtained at higher H_2/wax ratios.

Table 5
Model for isomers content of $C_{10–14}$ fraction

Coefficients	Value	Pr(>|*t*|)
Intercept	0.21452	<0.00000
Temperature	0.14367	<0.00000
Pressure	−0.02314	0.00010
WHSV	−0.06180	<0.00000
Temperature^2	0.05464	<0.00000
WHSV^2	0.02060	0.00010
Temperature:WHSV	−0.02866	0.00005

R^2: 0.98143, *F*: 151 on 6 and 21 degrees of freedom; *p*-value: 6.6613e−016.

Table 6
Model for the isomer content of $C_{15–22}$ fraction

Coefficients	Value	Pr(>|*t*|)
Intercept	0.45791	<0.00000
Temperature	0.15768	<0.00000
Pressure	−0.02627	<0.00000
WHSV	−0.06925	<0.00000
Temperature^2	0.03316	<0.00000
WHSV^2	0.01008	0.01541

R^2: 0.98653, *F*: 256.39 on 5 and 22 degrees of freedom; *p*-value: 0.

4. Conclusions

Adequate linear quadratic models describing the conversion of F–T wax and the isomer content of $C_{10–14}$ and $C_{15–22}$ fractions of the hydrocracking products in a wide range of operating conditions were determined. As for the overall conversion rate of C_{22+} fraction all factors investigated resulted to be meaningful with the biggest effect due to the temperature and the WHSV. Pressure and H_2/wax played a significant role as well. The effect of the latter can be rationalized assuming that with a feedstock characterized by a wide range of boiling point (i.e. 150–700 °C), VLE plays an important role in determining the apparent conversion rate and isomer content of products. The real situation from this standpoint is much more complex than the one considered in this paper because the cracking leads to a progressive lightening of the products and consequently to a change of the degree of vaporization during conversion. A more sophisticated approach is necessary for a detailed evaluation of VLE effect on hydrocracking.

A further facet which needs to be evaluated more closely is the interaction effect temperature–H_2/wax and temperature–WHSV.

Isomers content of middle distillate fraction of the products is of primary importance because directly linked to their cold flow properties. The models obtained show a good capability to fit the experimental data.

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