# A Kinetic Study of the Liquid Phase 2-ethyl-2-hexenal Hydrogenation over Ni-Cu/silica Catalyst

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*The hydrogenation of 2-ethyl-2-hexenal represents the last chemical step of the industrial process for synthesis of 2-ethylhexanol, an important commercial alcohol. The paper presents an experimental study of the liquid phase 2-ethyl-2-hexenal hydrogenation to 2-ethylhexanol over a commercial Ni/Cu - silica supported catalyst. The tests were performed in a laboratory autoclave, at typical conditions for the industrial process: reactant concentrations up to 30 % (wt), temperatures between 120 and 140 °C, pressures in the interval 12 – 35 bar and reactant (2-ethyl-2-hexenal) to catalyst weight ratios of 18 to 35. The results are evidencing a much higher rate of unsaturated >C=C< bond hydrogenation as compared with the hydrogenation of intermediary saturated aldehyde to alcohol. The rates of the two reactions were correlated to composition and temperature, by a power-law model.*

*Keywords: hydrogenation, 2-ethyl-2-hexenal, nickel-copper catalyst, batch experiments, kinetic model*

Today, 2-ethyhexanol is the most important superior alcohol, the worldwide production capacity totalizing $2.9 \cdot 10^6$ tons per year. Over 70% of this quantity is directed to the PVC plasticizers manufacture like classical dioctylphtalate (DOP) or newer 1,2,4-trioctyltrimellitate (TOTM); another 10% is consumed in the octylacrylate synthesis, a modern dyes component [1-2]. Industrial production of 2-etilhexanol consists in the catalytic hydrogenation of 2-ethyl-2-hexenal in either liquid or gas phase. Nickel Raney or supported catalysts are the only effective to catalyze the hydrogenation of the unsaturated aldehyde to the saturated alcohols [3-5]; others, like palladium, nickel sulfide or nickel boride complete the hydrogenation to saturated aldehyde state [5-8]. The main chemical reactions occurring in the catalytic hydrogenation process of 2-ethyl-2-hexenal are given in figure 1.

The commercial hydrogenation processes follow almost exclusively the two consecutive steps of the first route: 2-ethyl-2-hexenal → 2-ethylhexanal → 2-ethylhexanol, the carbon – carbon double bond being more reactive than carbon – oxygen double bond. Secondary reactions are also present in the process, with much smaller intensities. In liquid phase, the hydrogenation is generally more selective than in gas phase, traces of 2-ethyl-2-hexenol representing the major by-product detected.

In the open literature there are only few papers approaching the kinetics of 2-ethyl-2-hexenal hydrogenation. Smedler [6] and Niklasson and Smedler [7] investigated the gas phase hydrogenation of 2-ethyl-2-hexenal over Ni and Pd based catalysts, whereas the liquid phase hydrogenation kinetics on Ni, Pd and Ni-S catalysts was investigated by Smedler [8]. Due to the very small difference in normal boiling points (less than 2°C) between 2-ethylhexanol and 2-ethyl-2-hexenol, the removal of 2-ethyl-2-hexenol from 2-ethyhexanol on industrial scale succeeds only through hydrogenation in a dedicated (polish) reactor until complete consumption of the impurity. This feature represents the main shortcoming of the process. Using a high nickel concentration catalyst (56 wt% Ni on $SiO_2$) and pure 2-ethyl-2-hexenal as feedstock, Smedler [8] completed the most detailed and complex published kinetic study for 2-ethyl-2-hexenal liquid phase hydrogenation. Unfortunately, the experimental conditions used in this study are not very appropriate for per $C_8$ industrial hydrogenation requirements. The aim of this work is to investigate the kinetics of the 2-ethyl-2-hexenal hydrogenation, in conditions close to the currently industrial operated processes.

## Experimental part

The experiments were performed with 2-ethyl-2-hexenal having the purity of 97.2% (wt) and 2-ethylhexanol with a purity of 99.8 %, called hereinafter reactant and product respectively. The catalyst used was a commercial silica supported nickel/copper, currently used in industrial 2-ethyl-2-hexenal liquid phase hydrogenation. Prior to use, the commercial catalyst pellets were crushed, mechanically milled and classed on different size sieves. The fraction with size smaller than 50 μm, used in the

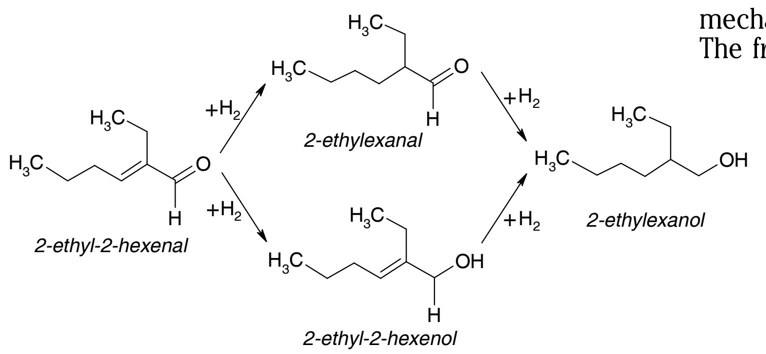

Fig. 1. The main chemical reactions occurring in 2-ethyl-2-hexenal hydrogenation to 2-ethyl hexanol

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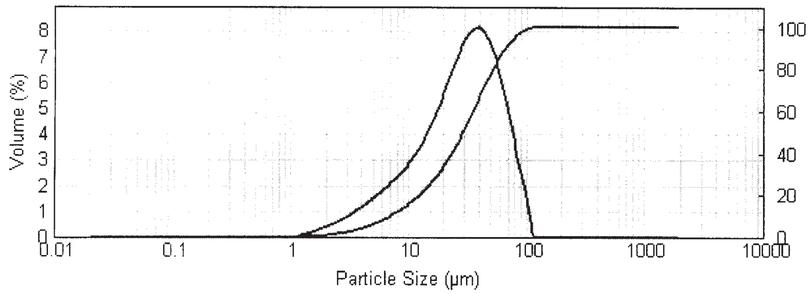

Fig. 2. Catalyst particle size distribution

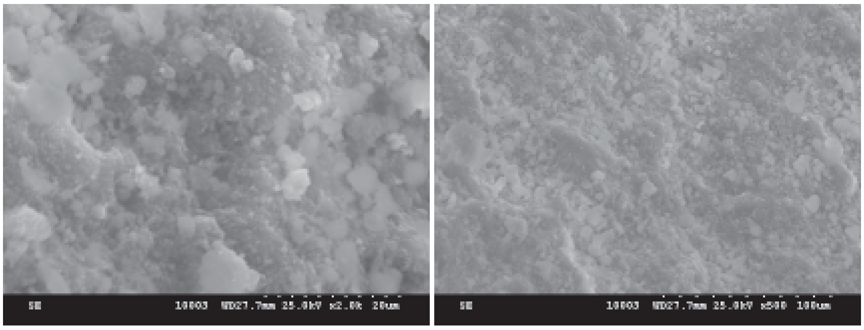

Fig. 3. SEM images of the catalyst

experiments, was analyzed with a particle size analyzer (Malvern, Mastersizer 2000). Water and iso-propanol were used as dispersants for solid particle with similar results. The particles size distribution of the catalyst used in the experiments is presented in figure 2, the mean diameter measured being 34 μm. The main chemical reactions occurring in 2-ethyl-2-hexenal hydrogenation to 2-ethyl hexanolm.

The structural morphology of the catalyst was evidenced by scanning electron microscopy (SEM), using a HITACHI S2600N apparatus. The catalyst samples images, presented in figure 3, shows a fairly good distribution of the nickel and copper species on support surface, most of microparticles having dimensions between 2 and 10 μm.

The measured specific surface area and average pore diameters of the catalyst were found to be 73.5 $m^2/g$ and 16.8 nm respectively, by the standard BET nitrogen absorption–desorption method (on a Micromeritics GEMINI apparatus). Isothermal absorption-desorption curves are shown in figure 4. Based on this analysis one can conclude that the analyzed material exhibits mesoporous characteristics, over 90% of the total pore volume being associated with mesopores (2-50 nm).

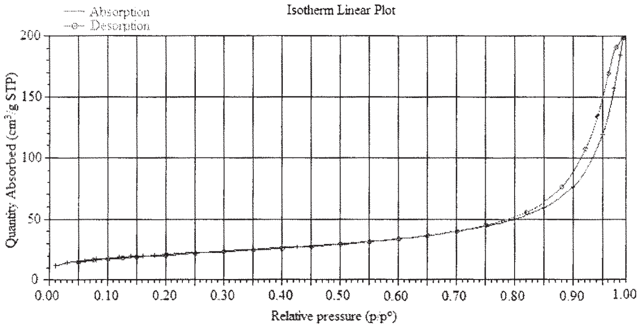

Fig. 4. Nitrogen absorption – desorption curves (BET)

The qualitative analysis of the catalyst composition was performed by energy dispersive X-ray spectroscopy (EDS). This analysis (fig. 5) evidenced that the sample contains Si, Cu and Ni (Ag is originating from the covering layer demanded by the SEM technique), the method not allowing distinguishing between metal and the corresponding metal compounds, like oxides. XRD analysis of the catalyst was performed using a Shimadzu XRD 6000 diffractometer at room temperature. In all the cases, the Cu Kα radiation from a Cu X-ray tube was used. The samples ground to fine powders were scanned in the Bragg angle (2θ) range of 10 – 87° at a scan rate of 2°/min. Accordingly to the XRD pattern (fig. 6) and the EDS elemental analysis, the following assumptions can be made: silicon is only in the amorphous silica form, while nickel and cooper are both in metallic and metal oxide forms, as proved by ASTM standard patterns.

Differential thermal analysis (DTA) coupled with thermogravimetric analysis (TGA) of the catalyst were performed in air atmosphere with a Shimadzu DTG-TA-50H, at a heating rate of 5°C/min. The TG-DTA spectrum (fig. 7) registered on the catalyst sample in air between 200 and 400° C, presents a mass growth of 2.47 %, corresponding most likely to Ni oxidation (exothermic process). In these conditions, the calculated nickel content in metal form is 9.05 %. Further, the UV-Vis spectroscopy was used to determine the nickel oxide content of the catalyst. In this aim, the sample was dissolved in ammonia solution and treated with dimethylglyoxime (alcoholic solution), to form a pink solution which can be determined at 410 nm by means of empirical recorded calibration curve. A 6.32 wt % Ni was so identified, present in catalyst as nickel oxide. Therefore, the total content of Ni amounts to 15.37%.

Cu was identified only as oxide through UV-Vis spectroscopy. A similar procedure as for Ni was used for Cu analysis, but without dimethylglyoxime as chelating agent, the bluish complex of Cu with ammonia being analyzed at 620 nm. The content of Cu was found to be 6.7 % as metal. The main catalyst properties are summarized in table 1.

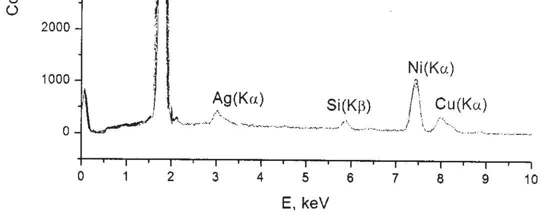

Fig. 5. EDS spectrum of the catalyst

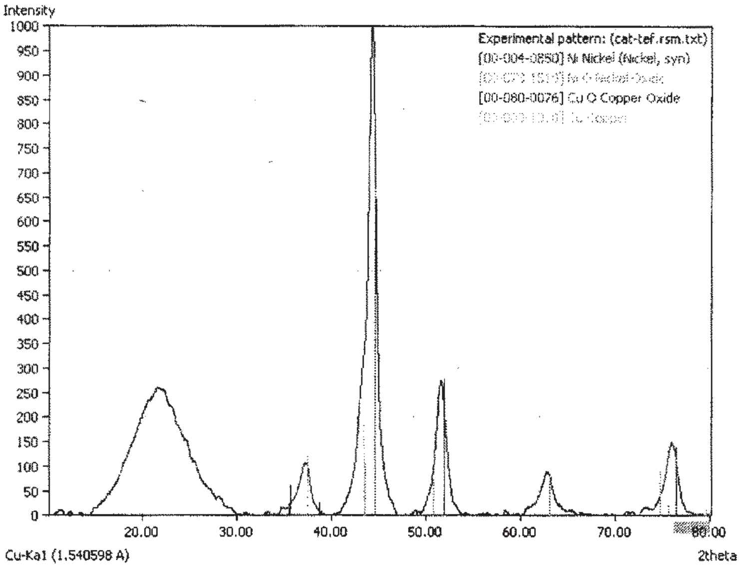

Fig. 6. XRD pattern of the catalyst

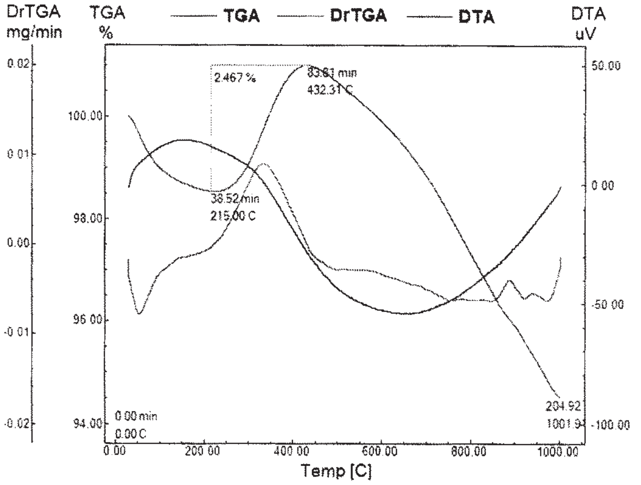

Fig. 7. TG-DTA analysis of the catalyst

*Hydrogenation experiments*

The liquid phase hydrogenation experiments were carried out in a 300 mL, high pressure, stainless steel batch reactor (BERGHOF). The reactor is provided with a heat transfer jacket, a magnetically driven mixing impeller and standard transmitters for internal pressure, temperature and impeller rotation frequency. The reaction temperature was controlled by circulating, in the reactor jacket, of a low volatility thermal oil, fed from a thermo-regulated bath. The reactor pressure is smoothly controlled (± 0.1 bar) by an electronic pressure controller, which is making-up fresh hydrogen from a cylinder, balancing in this way the hydrogen consumed in the hydrogenation process. Finally, a wide range speed controller (50 – 2000 rpm) is maintaining the impeller speed with high accuracy. The catalyst, reactant and product were loaded into reactor followed by a few pressurization-depressurization cycles with hydrogen to obtain an air free internal atmosphere. The catalyst – reaction mixture was heated under low hydrogen pressure up to desired reaction temperature. As soon as the reaction temperature was achieved, there was extracted a composition sample and the reactor was pressurized suddenly with hydrogen, this moment and composition being considered as reaction initial conditions. Further, there were collected, periodically, samples of reaction mixture. Before the analysis, the samples were centrifuged, to separate the solid catalyst. The clarified liquid samples were subsequently analyzed with a VARIAN CP 3800 gas-chromatograph equipped with a non-polar capillary column VARIAN CPSil-8CB, 50 m x 0.32 mm x 0.25 μm and FID detector. The method sensibility is good enough to detect the two isomers of the intermediate (2-ethyhexanal and 2-ethyhexenol), but, as mentioned in the first chapter, the unsaturated alcohol is contained in the reaction mixture only as traces. Several hydrogenation experiments replications on fresh catalyst charges evidenced a good process and analysis reproducibility. In addition, the reported compositions samples represent averages of two GC injections results.

To avoid the kinetic limitation of external diffusion, the stirrer speed was maintained at 1000 RPM for all experiments. To check the potential influence of internal

**Table 1**
HYDROGENATION CATALYST PROPERTIES

| **Property** | **Value** | **Analysis method** |
|---|---|---|
| *Macroscopic properties* | | |
| Particle mean size diameter | 34 μm | Wet size analysis |
| *Surface properties* | | |
| Superficial microscopic particle dimension | 2-10 μm | SEM |
| Specific surface | 73.5 $m^2/g$ | BET |
| Mean pores diameter | 16.8 nm | BET |
| *Composition* | | |
| Ni (as pure metal) | 15.37 % wt. | SEM-EDS, DTA-TGA, |
| Cu (as pure metal) | 6.7 % wt. | SEM-EDS, DTA-TGA, |
| $SiO_2$ | balance | SEM-EDS |

**Table 2**
EXPERIMENTAL CONDITIONS

| Parameter | Exp. #1 | Exp. #2 | Exp. #3 | Exp. #4 | Exp. #5 | Exp. #6 |
|---|---|---|---|---|---|---|
| Temperature [°C] | 130 | 140 | 120 | 130 | 130 | 130 |
| Pressure [Bar] | 33 | 33 | 33 | 27 | 18 | 12 |
| Initial concentration of 2-ethyl-2-hexenal (wt %) | 26.83 | 27.31 | 25.45 | 15.97 | 25.58 | 27.76 |
| 2-ethyl-2-hexenal to catalyst weight ratio | 31.8 | 34.39 | 31.86 | 18.22 | 18.84 | 19.2 |

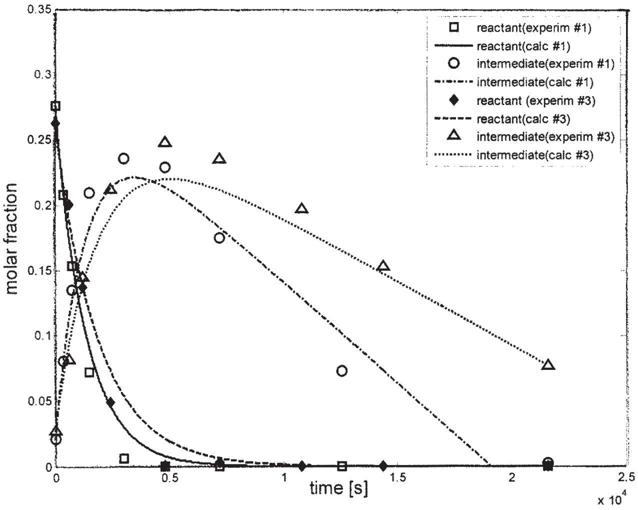

Fig. 8. Time evolutions of reactant and intermediate concentrations at different temperatures; points – experimental values and lines calculated values (hydrogen pressure 33 bar; reactant/catalyst wt ratio 31.8)

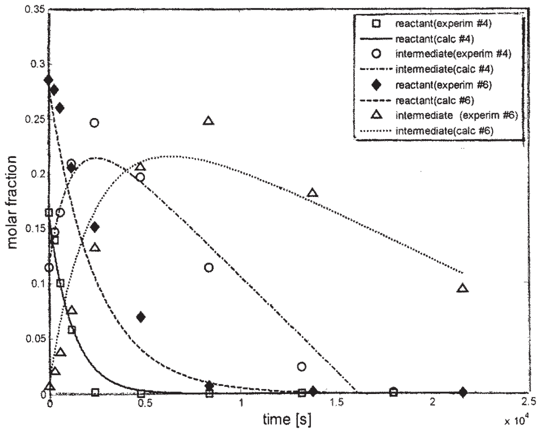

Fig. 9. Time evolutions of reactant and intermediate concentrations at different pressures; points – experimental values and lines calculated values (reaction temperature 130 °C, reactant/catalyst wt ratio ~19)

diffusion three catalyst particle dimensions were selected and tested (0-50, 50-106 and 106-212 μm) at the most severe conditions (130°C, 33 bar). In the experimental errors limits, the reactant (2-ethyl-2-hexenal) and the intermediate (2-ethylhexanal) concentrations showed similar evolution in time for catalyst batches of 0-50 and 50-106 μm particle dimensions. Consequently, catalyst particles having the size between 0-50 μm were used in the kinetic study.

## Results and discussions

In order to obtain data relevant for the industrial hydrogenation process of 2-ethyl-2-hexenal, as per ideas exposed in the introductory chapter, the experiments were designed to be relevant for the typical industrial conditions: reactant concentration below 30 % wt, temperature between 120–140°C and pressure up to 35 bar (table 2). Some experimental results are presented in figures 8 and 9, as discrete values of reactant and intermediate concentrations, at different reaction times. As expected, the increase of temperature or pressure is displacing the intermediate maximum toward smaller times and is reducing his amplitude. The results are evidencing that complete transformation of 2-ethyl-2-hexenal to 2-ethylhexanol, in diluted reactant mixtures specific for commercial applications, over the commercial Ni-Cu/silica catalyst, is achievable in reasonable reaction time values under hydrogen pressure higher than 33 bar, temperatures higher than 130 °C and 2-ethyl-2-hexenal to catalyst wt ratios around 32.

### *Development of a kinetic model for 2-ethyl-2-hexenal hydrogenation*

In the kinetic analysis, it was approximated the achievement of the physical gas – liquid equilibrium. As the liquid mixture is including only non-polar or slightly polar species, it was also hypothesized the ideal behaviour for both phases.

In these conditions, Henry and Raoult laws are usually used to calculate the gas (vapor)-liquid equilibrium:

$$y_i \cdot P = x_i \cdot Pvap_i \text{, (for reactant, intermediate, product and inert)} \quad (1)$$

$$y_i \cdot P = x_i \cdot H_i \quad \text{(for hydrogen)} \quad (2)$$

$$Pvap_i = \exp(a_i + \frac{b_i}{T} + c_i \cdot \ln(T) + d_i \cdot T^{e_i}) \quad (3)$$

$$H_i = a + \frac{b}{T} + c \cdot \ln(T) + d \cdot T + e \cdot T^2 + f \cdot T^3 \quad (4)$$

The constants for the temperature dependence of vapor pressure were taken from ASPEN simulator databank. The corresponding coefficients for Henry constant were calculated through non-linear regression based on the equilibrium data published in [9].

The rates of the two reactions involved in 2-ethy-2-hexenal hydrogenation to 2-ethylhexanol (fig. 1) were expressed as functions of composition and temperature, by a power law model. Preliminary calculations evidenced a weak dependence of the second hydrogenation step on the intermediate concentration. Collins and Grimes [3] also observed zero order kinetics for this reaction, in respect to the 2-ethyl-hexanal (over Raney Nickel catalyst). Therefore, the rate of the second reaction was considered as zero order in respect with the intermediate:

$$r_1 = k_1 \, C_{reactant} C_{hydrogen} \quad (5)$$

$$r_2 = k_2 \, C_{hydrogen} \quad (6)$$

$$k_i = k_{i0} \exp(\frac{-E_{ai}}{R}(\frac{1}{T} - \frac{1}{T_m})),\ i=1,2 \quad (7)$$

**Table 3**
ESTIMATED PARAMETERS VALUES

| Parameter | Value |
|---|---|
| *Rates constants values at $T_m$=403 K* | |
| $k_{10}$ [$m^6 \cdot kmol^{-1} \cdot kg^{-1} \cdot s^{-1}$] | $1.233 \cdot 10^{-3}$ (1 +/- 0.0615) |
| $k_{20}$ [$m^6 \cdot kmol^{-1} \cdot kg^{-1} \cdot s^{-1}$] | $1.355 \cdot 10^{-4}$ (1 +/- 0.0443) |
| *Activation energies* | |
| $E_{a1}/R$ [K] | 4881.2 (1 +/- 0.334) |
| $E_{a2}/R$ [K] | 6472.7 (1 +/- 0.183) |
| Correlation coefficient ($\rho^2$) | 0.97 |

In the above expression, $T_m$ is the average temperature of all experiments ($T_m$=403 K), $C_J$ is the molar concentration of species J and R the ideal gas constant. To describe the time evolution of the composition, there were used the mass balance equations:

$$\frac{d\xi_1}{dt} = m_{cat} r_1(\xi_1, \xi_2) \tag{8}$$

$$\frac{d\xi_2}{dt} = m_{cat} r_2(\xi_1, \xi_2) \tag{9}$$

$$t=0, \quad \xi_1 = \xi_2 = 0$$

$\xi_1$, $\xi_2$- the extents of the two reactions;
$m_{cat}$- the amount of catalyst.

The regression of kinetic parameters (activation energies and pre-exponential factors) was performed by the least squares method, using the MATLAB built-in function *lsqcurvefit*. The calculated parameters values and their 95% confidence intervals are given in table 3. The activation energy obtained in this study for the first reaction ($E_{a1}/R \cong 4880$ K), is close to the one published by Smedler [8] ($E_{a1}/R \cong 5500$ K), for a commercial Ni catalyst. The activation energy obtained for the second reaction ($E_{a2}/R \cong 6472$ K) is intermediary between the values published in the previous cited work ($E_{a2}/R \cong 9200$ K) and the one published by Collins and Grimes [3] for the same reaction catalyzed by Raney Nickel ($E_{a2}/R \cong 3615$ K).

In figures 8 and 9 are presented (by lines) the simulated time evolutions of the reactant and products species, corresponding to the proposed kinetic model. In addition, figure 10 presents a comparison between theoretical and experimental values of reactant and products concentrations, as a parity diagram. These graphical comparisons along with the correlation factor of 0.97 and the relatively tight 95 % confidence intervals of parameter values, demonstrate a good adequacy of the kinetic model to the experimental observations.

## Conclusions

The commercial Ni-Cu/silica catalyst features a relatively high activity and selectivity in the total hydrogenation of 2-ethy-2-hexenal to 2-ethyl hexanol. The experimental results obtained in this study, at compositions close to industrial ones, evidenced that total reactant conversion can be achieved in convenient reaction times, at temperatures over 130 °C and pressures over 30 bar. A power law kinetic model proved to be adequate to experimental data. The proposed power law kinetic model can be used in hydrogenation process analysis and design calculations.

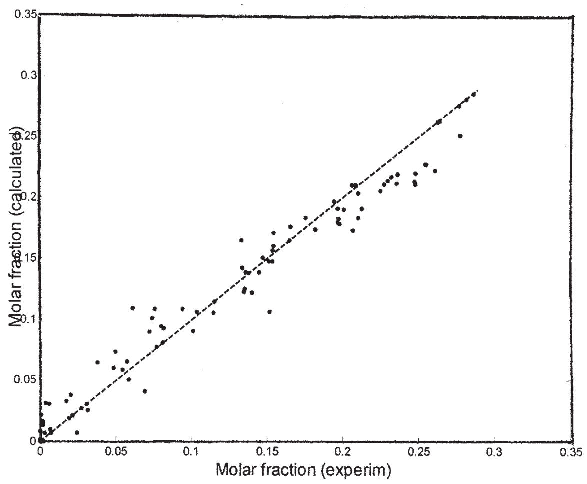

Fig. 10. Calculated versus eperimental concentration values for reactant and intermediate

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