



Short communication

Nickel removal from nickel-5,10,15,20-tetraphenylporphine using supercritical water in absence of catalyst: A basic study

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ABSTRACT

Reactions of nickel-5,10,15,20-tetraphenylporphine (Ni-TPP) were studied in supercritical water in the presence of toluene without the addition of any catalyst, H₂ or H₂S that is called a green process. The objective of this study was to remove nickel from Ni-TPP, the most common metal compound present in heavy crude, in high extent at low reaction time. All experiments were carried out in an 8.8 mL batch reactor fabricated from hastelloy C-276. The ability of supercritical water (SCW) to remove nickel from Ni-TPP was studied at temperatures of 450–490 °C and water partial pressures of 25–35 MPa. Water partial pressure had no effect on overall conversion at temperatures of 450 °C and a reaction time of 60 min. The overall Ni-TPP conversion was 89.80%, a figure above that of previous catalytic studies. The percentage of nickel removal was estimated as a function of reaction time and temperature. It were temperature 490 °C and pressure 25 MPa at reaction time 90 min where 65.68% nickel were removed by the action of SCW and toluene, as a co-solvent. It was determined that Ni-TPP undergoes a series of reactions, ending in demetallation and ring fragmentation. The obtained results suggest that supercritical water has a capability to remove nickel from Ni-TPP.

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1. Introduction

Refinement of heavy oils is necessary to meet increasing demand for lighter oils [1–5]. Heavy oils contain significant quantities of metals, mainly nickel, vanadium and iron, as well as sulfur and nitrogen heteroatom contaminants [4–6]. The concentration of vanadium is higher than that of nickel with few exceptions [5,6]. Nickel and vanadium are present in heavy oils forming porphyrinic structures [7,8]. Most studies to date have utilized porphyrin chelates [9,10]. There are basically four methods for the removal of metals from heavy oils and residuum fractions: physical, chemical, electrochemical and catalytic treatment processes [8,11]. The physical method removes a large amount of convertible material along with the metal-containing species. Chemical methods of demetallation involved selectively remove the metals from organic moiety by reaction with acids or alkali. This effort is at the laboratory to small pilot plant stages [11]. The only processes which have been proven capable of effecting substantial removal of metals are hydrotreating and gasification. Hydrotreating may not be economical or practical for heavy, high-metal content residues. Also, the metals contained in crude oil contaminate catalysts during the refining process [12]. The electrochemical process has successfully

removed metal under atmospheric pressure and room temperature reducing costs in the total process; however, direct demetallation in crude oil still remains as an open challenge for electrochemists [8].

Catalytic hydro-demetalation (HDM) process is the most used process for demetallation from crude oil and research results are available in open literature. It was Wei and co-workers [2–4,6,7] who pioneered HDM kinetics studies using model compounds. Later Weitkamp et al. [13], Chen and Massoth [14], Bonn  et al. [15,16] and Garcia-Lopez et al. [5] conducted additional studies. Hung and Wei [2], Agrawal and Wei [6], Ware and Wei [7], Garcia-Lopez et al. [5] studied reaction kinetics in the presence of unsulfided catalyst while Weitkamp et al. [13], Chen and Massoth [14], Bonn  et al. [15] carried out additional studies in the presence of sulfide catalyst. These researchers explored valuable study in the temperature ranges 125–400 °C. These efforts removed 90% metals implying high investment, operation cost and longer reaction time (8–9 h) [2–15]. It was Bonn  et al. [16] and Rankel [17] whom studied HDM reactions in the absence of a catalyst showing that conversion of Ni-TPP was low without a catalyst, but hydrogen sulfide has the capability to promote the conversion of Ni-TPP. The present works involve demetallation without catalyst, hydrogen or hydrogen sulfide addition for reducing operation cost, reaction time as a green process.

Supercritical water (SCW), water at a temperature and pressure above its critical points (374 °C and 22.1 MPa), is an attractive sol-

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vent as well as a hydrogen donor [1]. The ion product of water increases significantly at high temperatures and pressures. The dielectric constant of SCW ranges from 2 to 30, which are similar to the range of non-polar solvents (such as hexane, whose dielectric constant is 1.8), to polar solvents (such as methanol, whose dielectric constant is 32.6). With such a dramatic change of ion product and dielectric constant, SCW possesses either acidic or base effects on chemical reactions [18]. SCW also acts as a solvent and a reactant on hydrolysis-based reactions, and water molecules often take part as collision partners [19]. The effects of SCW on upgrading bitumen have been the subject of investigation [1]. However, no effective study on removing metal from heavy oil using supercritical water is available in literature. Such a method may become feasible as an environmentally benign process.

In this study, reactions of Ni-TPP in the presence of supercritical water at temperature ranges of 450–490 °C and at water partial pressures of 25–35 MPa in the absence of a catalyst and without the addition of hydrogen or hydrogen sulfide gas are reported.

2. Experimental

All experiments were carried out in an 8.8 mL batch reactor fabricated from hastelloy C-276. The reactor was designed and tested by AKICO (Tokyo, Japan) for a maximum temperature of 500 °C and maximum pressure of 50 MPa. No corrosion product was detected during control experiments at temperatures of 450 °C and 490 °C. Nickel-5,10,15,20-tetraphenylporphine (Ni-TPP) was used as a model compound as it is representative of the porphyrinic species found in crude oils [4,5]. The Ni-TPP was obtained from Sigma–Aldrich Japan K.K. and used without further treatment. Xylene (purity: 84%), encompassing ortho-, meta-, and para- isomers of dimethyl benzene, and toluene (purity: 99%) were purchased from Wako Pure Chemical Industries Ltd. and used without further treatment. Solvent grade xylene usually contains a small percentage of ethylbenzene as a contaminant. Bonn  et al. [15] have reported that Ni-TPP has poor solubility in xylene at room temperature. Thus, a sufficient amount of xylene was added to dissolve Ni-TPP with the other reaction species.

Approximately 0.02 g of Ni-TPP, 0.82–0.96 mL of distilled water and 1 mL of toluene were loaded to the batch type reactor for supercritical water reactions. Water partial pressures at constant temperature and reactor volume were controlled by controlling the amount of water loaded into the reactor. Software, water I, v.3.3, produced by Summit Research Corporation (1996) was used to compute the amount of water by fixing temperature and water partial pressure. Exact amount of water was loaded during experiments. The reactor was reassembled and argon gas was used to purge the reactor of gas at a pressure of 0.80 MPa. An electric furnace, made by AKICO (Tokyo, Japan), was heated to the planned temperature and the reactor was then loaded to the furnace. After loading the reactor, the temperature of the furnace decreased slightly for a short period, and subsequently started to increase again. This study defines zero reaction time as the time when the temperature of the furnace started to increase again after the reactor was loaded. During each run, the reactor was shaken in a front–back motion at approximately 70 cycles per minute, a rate sufficient to cause the reactor interior temperature to increase quickly. After a specific reaction period, the furnace was stopped and the reactor was removed from the furnace and quenched in an ice bath. The reactor was then opened and water was separated using a separating funnel. Finally, the reaction products were collected by washing with xylene.

2.1. Analysis

Ultraviolet–visible (UV–vis) spectrophotometric analyses were performed on a spectrophotometer, Shimadzu (Model UV-1200) using a 12.5 mm × 12.5 mm × 45 mm cuvette and xylene as a solvent. The samples were scanned from 400 nm to 800 nm. The UV–vis spectrophotometer was used to determine the concentrations of the porphyrinic reactant as well as the reactant intermediates in the liquid samples. The concentrations of the porphyrin and its hydrogenated intermediate compounds were computed applying the Lambert–Beer law. The molar absorptivity coefficient (ϵ) for Ni-TPP was estimated from the calibration curve made from standard solutions of pure compound. The absorption coefficients of the intermediate compounds, Ni-TPC and Ni-TPiB, were calculated using the absorbance versus time curves of data from literature [5,16]. As the absorption coefficient of Ni-TPHP and Ni-TPB are not available in open literature [16], it was not possible to calculate the absolute concentrations of these compounds. The total nickel content of the samples was analyzed by Atomic Absorption Spectrophotometer (AAS) (Shimadzu AA-6800). The samples were dissolved in xylene and then charged to the AAS auto sampler. The data were acquired and reduced by computer software. Definitions of the terms used in this study are given below:

The conversion of Ni-TPP is defined as:

$$\text{Conversion (\%)} = \frac{W_{o,\text{Ni-TPP}} - W_{\text{Ni-TPP}}}{W_{o,\text{Ni-TPP}}} \times 100 \quad (1)$$

where $W_{o,\text{Ni-TPP}}$ = weight of Ni-TPP loaded and $W_{\text{Ni-TPP}}$ = weight of Ni-TPP unreacted at reaction time t

Percentage of nickel removal is defined as:

$$\text{Nickel removal (\%)} = \frac{W_{o,\text{Ni}} - WP_{\text{Ni}}}{WP_{\text{Ni}}} \times 100 \quad (2)$$

where $WP_{o,\text{Ni}}$ = initial percentage of nickel present in loaded Ni-TPP and WP_{Ni} = percentage of nickel present in the samples at time t

The yield of product is defined as:

$$\text{Yield (\%)} = \frac{W_{i,\text{IC}}}{W_{o,\text{Ni-TPP}}} \times 100 \quad (3)$$

where $W_{i,\text{IC}}$ = weight of intermediate compounds ($i = 1, 2, 4$) and $W_{o,\text{Ni-TPP}}$ = weight of Ni-TPP loaded

3. Results and discussion

3.1. Product distribution

As mentioned above, most previous research has focused on catalytic reactions, with the exception of Rankel [17] and Bonn  et al. [16]. Rankel studied thermal degradation of H₂-TPP, Ni-TPP and VO-TPP at 240 °C in refluxing 1-methylnaphthalene in the presence of H₂ and H₂S and concluded that the reactivity follows the order: H₂-TPP > Ni-TPP > VO-TPP. Bonn  et al. also noted the same reactivity order at 287 °C. It is clear that the central metal group has a stabilizing influence on the porphyrin macrocycle with respect to hydrogenation reactions and ring fragmentation. Bonn  et al. showed that Ni-TPP conversion was close to 4% in the absence of H₂S, but it was close to 18% in its presence at 320 °C and a reaction time of about 6 h. In the presence of a sulfide catalyst (Mo/Al₂O₃) conversion of Ni-TPP was close to 50% under the same conditions. Bonn  et al. [15] also found in a separate catalytic study that H₂S promotes demetallation.

Ni-TPP is a solid crystal and purple in color. It is insoluble in water, but soluble in xylene and toluene. The xylene-soluble Ni-TPP is red in color and has intensive absorption peaks in the visible band. A typical VIS spectrum of pure Ni-TPP exhibits several characteristics. A Soret band, a typical feature of all porphyrin compounds

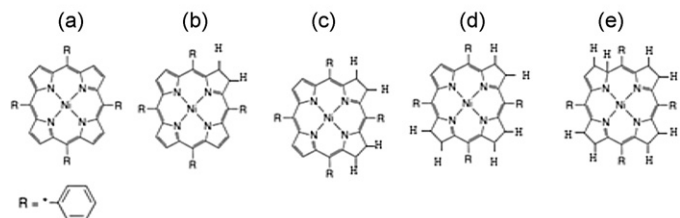
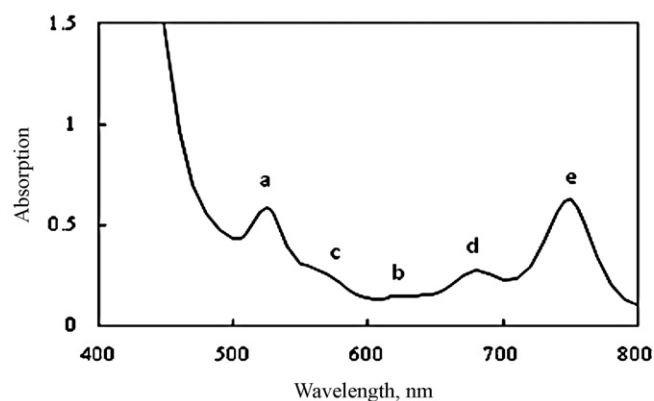


Fig. 1. VIS-spectra of reaction samples at a temperature of 450 °C, a pressure of 25 MPa where (a) nickel-5,10,15,20-tetraphenylporphine (Ni-TPP), (b) nickel-5,10,15,20-tetraphenylchlorin (Ni-TPC), (c) nickel-5,10,15,20-tetraphenylisobacteriochlorin (Ni-TPiB), (d) nickel-5,10,15,20-tetraphenylhexahydroporphyrin (Ni-TPHP), (e) nickel-5,10,15,20-tetraphenylbacteriochlorin (Ni-TPB).

[9], was observed at about 414 nm. Based on literature data the absorption band at 527.5 nm (a) was assigned to Ni-TPP and used for quantitative analysis as it offered the best calibration curves. The peak at 616 nm (b) was assigned to its hydrogenated form nickel-5,10,15,20-tetraphenylchlorin (Ni-TPC), which was present as a contaminant. VIS-spectrum of samples from experiments with Ni-TPP at 450 °C is shown in Fig. 1, exhibits three new peaks. The peak at 595 nm (c) is a characteristic absorption of nickel-5,10,15,20-tetraphenylisobacteriochlorin (Ni-TPiB). Bonn e et al. [16] reported that the peaks at 680 nm (d) and 750 nm (e) are tentatively assigned to nickel-5,10,15,20-tetraphenylhexahydroporphyrin (Ni-TPHP) and nickel-5,10,15,20-tetraphenylbacteriochlorin (Ni-TPB) respectively.

3.2. Reactions of Ni-TPP with supercritical water in toluene environment

Four runs were performed with supercritical water without catalysts to investigate the effects of water partial pressure at a temperature of 450 °C and pressures of 25–35 MPa in a toluene environment. Pressure appears to have no significant effect on overall conversion. The error margin of the acquired data was less than 2%.

A plot of conversion of Ni-TPP as a function of reaction time at temperatures of 450–490 °C and water partial pressure of 25 MPa is shown in Fig. 2. A continuous increase in Ni-TPP conversion was observed over reaction times of 30–90 min. At a reaction time of 90 min and a temperature of 490 °C, the conversion was 89.80%, a figure greater than even the catalytic conversion at a temperature of 320 °C as shown by Bonn e et al. [16].

Fig. 3 shows overall nickel balance at temperatures of 450–490 °C. Nickel removal was shown to be low at low reaction times but increased with time. The nickel removal rate was higher at a temperature of 490 °C and the value reached 65.63% after a reaction time of 90 min. Bonn e et al. [16] has reported that the fate of the central metal groups after demetallation under non-catalytic

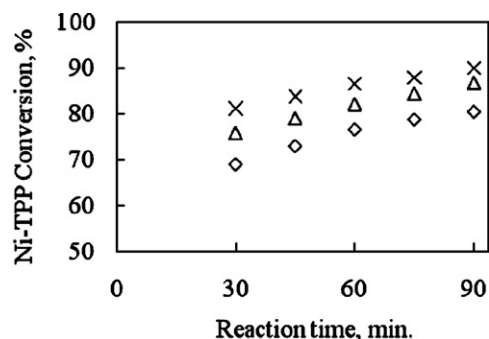


Fig. 2. Conversion of Ni-TPP as a function of reaction time at different temperatures (\diamond , 450 °C; Δ , 470 °C; \times , 490 °C).

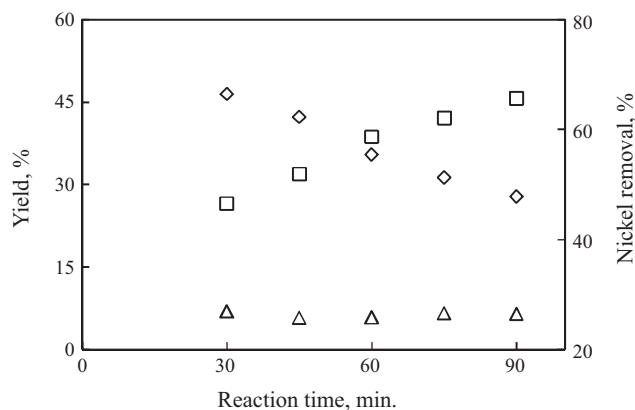
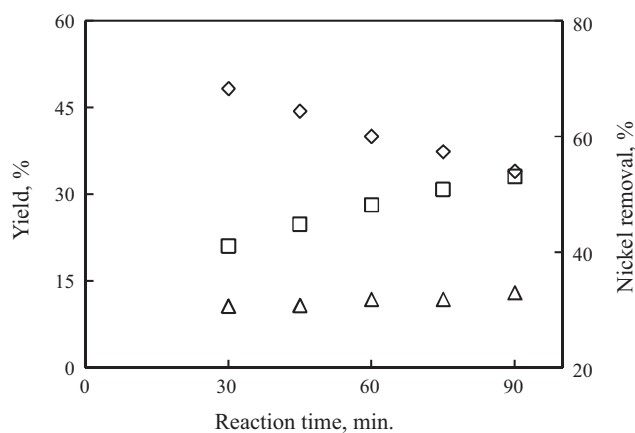
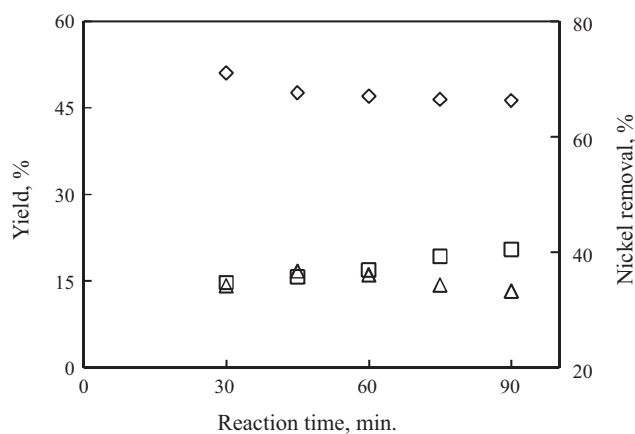


Fig. 3. Overall nickel balance: (a, top), 450 °C; (b, middle), 470 °C; (c, bottom), 490 °C (\square , nickel removal; \diamond , total nickel in Ni-TPP, Ni-TPiB and Ni-TPC form; Δ , total nickel in the samples in other form).

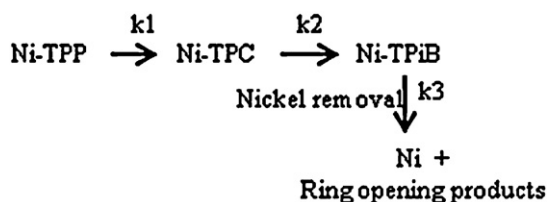


Fig. 4. Possible reaction sequence for Ni-TPP.

Table 1
Kinetic parameters.

Temperature (°C)	Rate coefficient (min ⁻¹)		
	k_1	k_2	k_3
450	0.0212	0.0019	0.0027
470	0.0261	0.0032	0.0043
490	0.0299	0.0037	0.0058
Activation energy (Kcal/mol)			
E_1	4.06		
E_2	7.97		
E_3	9.11		

conditions remains obscure. The fate of the central metal groups in reaction of Ni-TPP under supercritical condition was also obscure as a result of our experiment, though formation of metal hydroxides, metal oxides and metal ions are a possibility. A maximum 16.04% of nickel was present in the samples except for the Ni-TPP, Ni-TPiB and Ni-TPC forms. These forms include Ni-TPHP and Ni-TPB. Thus, Ni-TPHP and Ni-TPB were not included in the reaction pathways. The yields of Ni-TPC, Ni-TPiB, Ni-TPHP and Ni-TPB increased rapidly, reaching a maximum value before decreasing to a minimum value; this indicates that these were intermediates compounds [16].

3.3. Reaction kinetics and pathways

The kinetics of Ni-TPP demetallation is modelled as a sequence of pseudo-first order reactions in the network shown in Fig. 4 based on experimental results with the help of literature proposed by Ware and Wei [7] and Bonné et al. [16]. According to the chemistry of metalloporphyrins, Ni-TPP is hydrogenated several times successively under conditions of chemical reduction until the macromolecule of porphyrin is broken, losing its porphyrinic character [5]. Thus, feed porphyrin was successively hydrogenated to form the tetrahydro species. This Ni-TPiB then released metal through hydrogenolysis and ring fragmentation phenomena. Rate coefficients were determined with the help of Himmelblau et al. techniques [20]. The initial hydrogenation of Ni-TPP was rapid, and the second hydrogenation step was rate determining in the demetallation sequence. The activation energies, obtained from Arrhenius plot, for the first hydrogenation step (k_1), second hydrogenation step (k_2) and hydrogenolysis (k_3) step were 4.06, 7.97 and 9.11 kcal/mol respectively (Table 1).

4. Conclusions

Ni-TPP was reactive with supercritical water, which was also a source of hydrogen donor and a catalyst. Experimental results

revealed that about 89.80% of the Ni-TPP was converted to intermediate and final products at a temperature of 490 °C, a pressure of 25 MPa and a reaction time of 90 min. Under the same conditions, around 65.63% nickel was removed by the action of supercritical water. Overall Ni-TPP conversion was basically invariant at the change of water partial pressure. Nevertheless, supercritical water was capable of removing nickel from Ni-TPP.

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References

- [1] M. Watanabe, S.N. Kato, S. Ishizeki, H. Inomata, R.L. Smith Jr., Heavy oil upgrading in the presence of high density water: basic study, *J. Supercrit. Fluids* 53 (2010) 48–52.
- [2] C.W. Hung, J. Wei, The kinetics of porphyrin hydrodemetallation. 1. Nickel compounds, *Ind. Eng. Chem. Process Des. Dev.* 19 (1980) 250–257.
- [3] C.W. Hung, J. Wei, The kinetics of porphyrin hydrodemetallation. 1. Vanadyl compounds, *Ind. Eng. Chem. Process Des. Dev.* 19 (1980) 257–263.
- [4] B.J. Smith, J. Wei, Deactivation in catalytic hydrodemetallation. 1. Model compound kinetic studies, *J. Catal.* 132 (1991) 1–20.
- [5] A.J. Garcia-Lopez, R. Cuevas, J. Ramirez, J. Ancheyta, A.A. Vargas-Tah, R. Naves, A. Gutierrez-Alejandre, Hydrodemetallation (HDM) kinetics of Ni-TPP over Mo/Al₂O₃-TiO₂ catalyst, *Catal. Today* 107–108 (2005) 545–550.
- [6] R. Agrawal, J. Wei, Hydrodemetallation of nickel and vanadium porphyrins. 1. Intrinsic kinetics, *Ind. Eng. Chem. Process Des. Dev.* 23 (1984) 505–514.
- [7] R.A. Ware, J. Wei, Catalytic hydrodemetallation of nickel porphyrins I. Porphyrin structure and reactivity, *J. Catal.* 93 (1985) 100–121.
- [8] K. Welter, E. Salazar, Y. Balladores, O.P. Marquez, J. Marquez, Y. Martinez, Electrochemical removal of metals from crude oil samples, *Fuel Process. Technol.* 90 (2009) 212–221.
- [9] N. Marquez, F. Ysambertt, C.D.L. Cruz, Three analytical methods to isolate and characterize vanadium and nickel porphyrins from heavy crude oil, *Anal. Chim. Acta* 395 (1999) 343–349.
- [10] M.F. Ali, H. Perzanowski, A. Bukhari, A.A. Al-Haji, Nickel and vanadyl porphyrins in Saudi Arabian crude oils, *Energy Fuels* 7 (1993) 179–184.
- [11] M.F. Ali, S. Abbas, A review of methods for the demetallization of residual fuel oils, *Fuel Process. Technol.* 87 (2006) 573–584.
- [12] F.X. Long, B.S. Gevert, Kinetics of vanadyl etioporphyrin hydrodemetallation, *J. Catal.* 200 (2001) 91–98.
- [13] J. Weitkamp, G. Wolfgang, R. Rolf, D. Harald, Model studies for catalytic hydrodemetallization at low temperatures, *Erdoel Kohle, Ergas Petrochem.* 36 (12) (1983) 569–574.
- [14] H.J. Chen, E. Massoth, Hydrodemetallation of vanadium and nickel porphyrins over sulfided CoMo/Al₂O₃ catalyst, *Ind. Eng. Chem. Res.* 27 (1988) 1629–1639.
- [15] R.L.C. Bonné, P. van Steenderen, A.E. van Diepen, J.A. Moulijn, Hydrodemetallation of nickel-5,10,15,20-tetraphenylporphyrin over sulphided Mo/Al₂O₃: initial catalyst deactivation, *Appl. Catal. A. Gen.* 108 (1994) 171–186.
- [16] R.L.C. Bonné, P. van Steenderen, J.A. Moulijn, Hydrogenation of nickel and vanadyl tetraphenylporphyrin in absence of a catalyst: a kinetic study, *Appl. Catal. A. Gen.* 206 (2001) 171–181.
- [17] L.A. Rinkel, Reactions of metalloporphyrins and petroporphyrins with H₂S and H₂, *ACS Prepr. Div. Petr. Chem.* 26 (1981) 689–698.
- [18] O.M. Ogunsola, Decomposition of isoquinoline and quinoline by supercritical water, *J. Hazard. Mater.* 74 (3) (2000) 187–195.
- [19] S. Takafumi, T. Adschiri, K. Arai, Decomposition kinetics of 2-propylphenol in supercritical water, *J. Anal. Appl. Pyrolysis* 70 (2003) 735–746.
- [20] D.M. Himmelblau, C.R. Jones, K.B. Bischoff, Determination of rate constants for complex kinetic models, *Ind. Eng. Chem. Fundam.* 6 (4) (1967) 539–543.