

## Modelling the Two-Stage Pyrolysis Gasoline Hydrogenation

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### Abstract

A model is developed based on a two-stage hydrogenation of pyrolysis gasoline to obtain a C<sub>6</sub>-C<sub>8</sub> cut suitable for extraction of aromatics. The first stage hydrogenation takes place in a trickle bed reactor while the second stage hydrogenation is carried out in a two compartment fixed bed reactor in which hydrogenation of olefins takes place in the first compartment while the sulphur is eliminated in the second compartment. The key component in this stage is considered to be cyclohexene whose hydrogenation was found to be the most difficult among other olefins in the feed. The Langmuir-Hinshelwood kinetic expression was adopted for hydrogenation of cyclohexene and its kinetic parameters were determined experimentally in a micro-reactor. The model was solved for the whole process of hydrogenation, including hydro-desulphurization. The predictions of the model were compared with the actual plant data of an industrial scale pyrolysis gasoline hydrogenation unit and satisfactory agreement was found between the model and the plant data.

**Keywords:** pyrolysis gasoline, hydrogenation, reactor modelling

### 1. Introduction

The pyrolysis gasoline, which is a by-product in the olefin plants, has a high content of unsaturated components such as olefins and di-olefins. The existence of these unstable components prevents the occurrence of desulphurization at high temperatures. Furthermore, under such conditions, fouling occurs due to polymer being deposited on both the catalyst and the equipments. Therefore, the pyrolysis gasoline is hydrogenated in a two-stage process to resolve these difficulties. In addition, the pyrolysis gasoline should be practically free of sulphur compounds. In the first stage, a selective hydrogenation of di-olefins to mono-olefins takes place, while at the second stage, the hydrogenation of the mono-olefins to saturated hydrocarbons would be completed.

An attempt has been made in this work to simulate the two stage pyrolysis gasoline hydrogenation process based on the information found in the literature and the results of the experiments conducted during the study. Some plant data are also used to evaluate the performance of the model proposed in the present study.

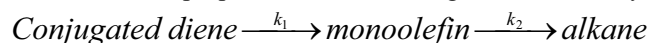
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## 2. Kinetics

### 2.1 First stage reactor

In the first stage reactor, di-olefins are being hydrogenated. Cheng et al. (1986) studied the kinetics of pyrolysis gasoline hydrogenation over the supported palladium catalyst. The hydrogenation reaction is proposed as the following consecutive way:



Cheng et al. (1986) found that the kinetic rate constants  $k_1^*$  and  $k_2^*$  are equal to 132 and 37 mL.g<sup>-1</sup>.hr<sup>-1</sup>, respectively. The big difference between these values indicates that hydrogenation of conjugated dienes can be selectively controlled to favour of mono-olefin formation at the reaction conditions.

Hanika and Lederer (1999) also studied the kinetics of pyrolysis gasoline hydrogenation. Typical pyrolysis gasoline contains C<sub>5</sub>-C<sub>12</sub> hydrocarbons and specially is rich in C<sub>5</sub>-C<sub>6</sub> cut. Accordingly, Hanika and Lederer (1999) considered 18 individual reactions for selective hydrogenation of diens, using Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.

The following assumptions have been considered in this work for the first stage reactions kinetics:

- Eighteen reactions reported by Hanika and Lederer (1999) were used to model the first stage reactor. The rate constants are considered to be the same as those reported by Hanika and Lederer (1999). However, in the absence of information about the activation energies, these values are considered to be the same as that reported by Cheng et al. (1986) who studied the same reaction system.
- The activation energy and reaction rate constants for styrene and isoprene hydrogenation are obtained from Cheng et al. (1986).

### 2.2 Second stage reactor

In the second stage reactor hydro-treating of mono-olefin components and desulphurization are performed. The feed to this stage is the C<sub>6</sub> cut from the first stage reactor. The reactor consists of two fixed catalyst beds in series. In the first bed, mono-olefins are hydrogenated while desulphurization is occurred in the second bed. As mentioned above, cyclohexene is the key component in the C<sub>6</sub> cut. Hydrogenation of cyclohexene produces cyclohexane as the main product. The catalyst in this bed is Ni-Mo/Al<sub>2</sub>O<sub>3</sub>.

Qu and Prins (2002) showed that the order of hydrogenation reaction of cyclohexene is between zero and one. Therefore, a Langmuir-Henshilwood expression was selected for the kinetics of cyclohexene hydrogenation as follows:

$$-r = \frac{kK_H P_H}{1 + K_H P_H} \quad (1)$$

In the second bed of the second stage, sulphur is removed from the pyrolysis gasoline by reaction with hydrogen. Since the C<sub>6</sub> cut has a narrow boiling point range, it could be assumed that thiophene, which has almost the boiling point of the C<sub>6</sub> cut, is the main sulphur compound in this cut. Thiophene disappearance due to hydro-desulphurization is given as follows (Gianetto and Silveston, 1986):

$$r_{HDS} = \frac{k'_T P_T P_{H_2}}{(1 + K_T P_T + K_{H_2S} P_{H_2S})^2} \quad (2)$$

### 3. Experimental

#### 3.1 Materials and catalyst

The chemicals employed in the experiments were hydrogen (purity>99.99%), nitrogen (purity>99.99%); iso-octane (purity>99%) as solvent; cyclohexene (purity>99%). The Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst sample was supplied by Procatalyse Co. (LD 145). The sample was crushed and sieved to obtain catalyst particles ranged from 300-600 μm.

#### 3.2 Apparatus and procedure

A schematic diagram of the experimental set-up is shown in Figure 1. Nitrogen was passed through cyclohexene to have nitrogen gas saturated with cyclohexene vapour to form the feed stream. Temperature of cyclohexene container was controlled by a water bath equipped with temperature controller and heater. Hydrogen was fed to the reactor simultaneously. The reactor consisted of a 6.3 mm I.D. U-shaped stainless steel tube containing 0.9 g of commercial Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. The hydrogenation was carried out at atmospheric pressure. The surrounding temperature of the reactor was kept constant by a melt salt bath equipped with temperature controller and heater.

The experiments were carried out at 190, 240 and 290 °C according to the industrial conditions. Different partial pressures of cyclohexene hydrogenation were used at different temperatures with varying feed flow in order to achieve a wide range of cyclohexene hydrogenation conversions. Composition of the feed and product was analyzed using a gas chromatograph.

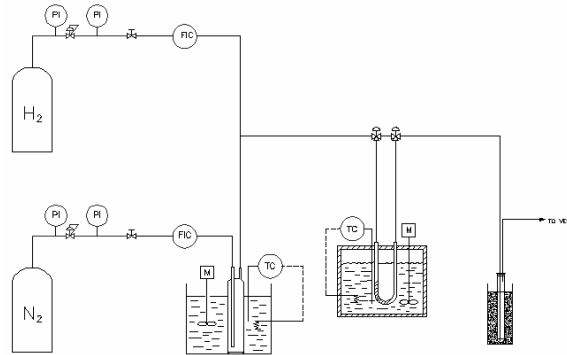


Figure 1: Schematic of the experimental set-up for cyclohexene hydrogenation A=Regulator, B=Saturator, C=Reactor, PI=Pressure indicator, FIC=Rotameter, TC=Temperature controller

### 4. Model Development

#### 4.1 First stage reactor

The first stage reactor is a trickle bed. The model equations for the first stage reactor are:

Mass balance:

$$\frac{1}{A} \frac{dF_{l,i}}{dz} + f_w a_c (k_{ls})_i (C_{l,i} - C_{s,i}) = 0 \quad (3)$$

Liquid-catalyst mass transfer:

$$a_c (k_{ls})_i (C_{l,i} - C_{s,i}) = \rho_b \sum_{i=1}^n v_i r_i \quad (4)$$

Energy balance:

$$\frac{F}{A} C_{P_i} \frac{dT}{dz} = \sum \Delta H_i r_i \quad (5)$$

The correlations used in this work for evaluating the hydrodynamic parameters of the trickled bed were adapted from Holub et al. (1992) for pressure drop, Larachi et al. (1991) for liquid hold-up, Al-Dahhan, and Dudukovic (1995) for catalyst wetting efficiency and Lakota and Levec (1990) for liquid-solid mass transfer coefficient.

#### 4.2 Second stage reactor

The second stage reactor is a gas-phase fixed bed reactor which could be modelled by the following equations:

Mass balance:

$$\frac{1}{A} \frac{dF_i}{dz} = \rho_b \sum_{i=1}^n v_i r_i \quad (6)$$

Energy balance:

$$\frac{F}{A} C_{P_i} \frac{dT}{dz} = \sum \Delta H_i r_i \quad (7)$$

## 5. Results and Discussion

### 5.1 Experimental

The Arrhenius and Van't Hoff laws were considered for the reaction rate constants  $k$  and adsorption constant  $K_H$ , respectively. From the experimental results obtained at different temperatures in this work, the temperature dependence of the reaction rate and adsorption equilibrium constants were calculated. Table 1 shows the fitted parameters for hydrogenation of cyclohexene to cyclohexane over the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst based on the experimental data obtained in this work.

Table 1 : Constants of kinetic rate and adsorption constants for cyclohexene hydrogenation

Parameter	Unit	Value	Standard deviation
$k_0$	mol/gr cat./min	0.178	0.012
$E_a$	kJ/mol	40.47	2.62
$K_{H0}$	kPa <sup>-1</sup>	29.89	1.00
$\Delta H$	kJ/mol	-24.48	1.48

## 5.2 Modelling

The model equations for both reactors were solved for an industrial unit. The reactors at each stage consist of two packed beds in series (located in a single vessel) and a quench space is foreseen between these beds for cooling the product of the first bed.

Figure 2 illustrates the calculated and measured axial temperature profiles of the first stage reactor. The circles in this figure are the plant data and the solid line represents the results of simulation. It is seen in this figure that the temperature increases along the reactor length due to exothermic hydrogenation of diens. It is obvious from this figure that there is a good agreement between the model predictions and actual plant data for this reactor.

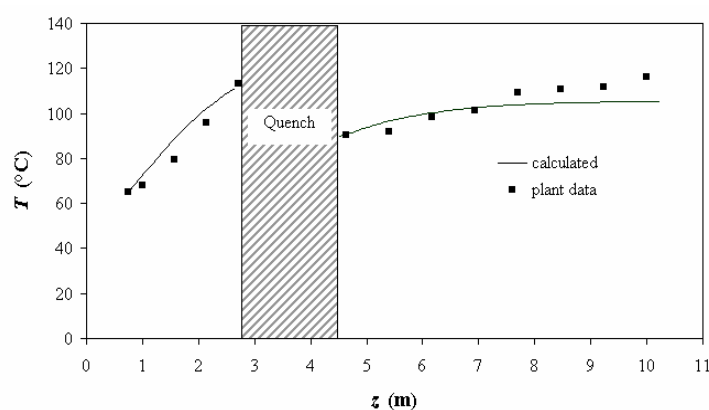


Figure 2. Axial temperature profile in the 1<sup>st</sup> stage reactor

Calculated and plant axial profile of temperature in the second stage reactor is shown in Figure 3. It is seen in this figure that a very good agreement exists between the calculated temperatures and plant data in both beds. The change in the temperature in the first bed is due to hydrogenation of olefins to alkanes while in the second bed, this change corresponds to hydrodesulphurization of the feed.

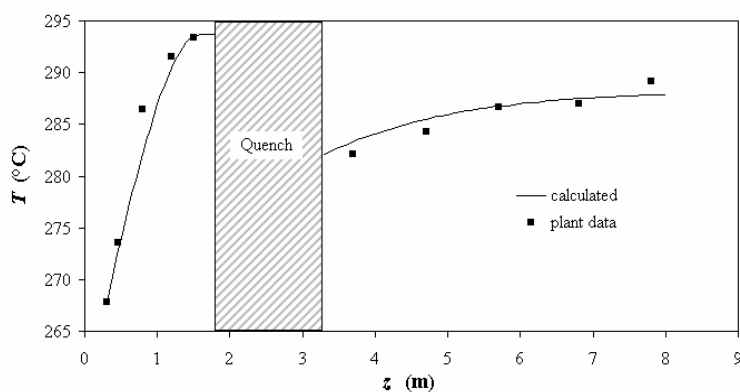


Figure 3. Axial temperature profile in the 2<sup>nd</sup> stage reactor

As discussed earlier, thiophene is considered to be the sulphur containing component of pyrolysis gasoline. It was found that sulphur is removed effectively from the feed in this reactor (Ahmadpour, 2003).

## 6. Conclusions

A model was developed for modelling the process of pyrolysis gasoline hydrogenation. The proposed model integrates hydrodynamic parameters and kinetic models necessary to simulate such a process. For modelling the first stage of hydrogenation, in which dienes are completely removed from the feed, the kinetic expressions from the literatures were used. In the second stage of hydrogenation, the olefins are removed from the feed by hydrogenation to alkanes in the first bed. The reaction rate of this process is experimentally determined in this work by investigating hydrogenation of cyclohexene to cyclohexane. Hydrodesulphurization of the feed occurs in the second bed of the second stage hydrogenation reactor. For the modelling purpose, the sulphur-containing component of the pyrolysis gasoline is assumed to be thiophene whose hydrogenation rate is found in the literatures. The validity of the model was demonstrated by comparing the model predictions with plant data in terms of temperature profiles in both first and second stage reactors. Very good agreement between the predictions of the model developed in this study and the actual industrial reactor data is obtained. The results of this study can be used as a framework to further development of PGH processes.

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