

Approach to Kinetic Modelling for Syngas Production from Heptane and Water

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Abstract- In the field of electric generation, the possibility of converting liquid to gaseous fuels is of great importance for more efficient and clean processing. For this reason, a broad kinetic study is being conducted by the authors in order to replicate its results on an industrial scale. This work presents a simple kinetic model developed for the reaction between heptane and water in an experimental reactor maintained at 500°C. The obtained model and experimental results will first be extended by changing the reaction temperature and the reagent-ratio, and later through the study of other hydrocarbons (both pure and in a mixture). Such information will also be integrated with that coming from a parallel study by the same authors about the gaseous production from solid biomass.

Keywords- heptane; kinetics; syngas.

I. INTRODUCTION

In recent years many efforts have been devoted to finding better solutions for the efficient processing of biomass and organic fuels, so as to obtain large and small scale electricity generation. Most of these efforts have been addressed to hydrogen production to be used in fuel cells [1-3], but this generally requires the fuel to have strict pureness characteristics. Processing liquid fuels can present some disadvantages, both from the technical and economic point of view, and similar problems are connected with the use of solid fuels, such as untreated biomass [4]. Obviously, operating with conversion from solid biomass to oils can encounter the same problems as those occurring when processing liquid fuels. Syngas production processes, such as fast pyrolysis, seem to be promising in generating electricity from biomass, since gaseous fuels can be used either in a turbine or in an internal combustion engine [4]. Great attention has also been devoted to hydro processing in biofuel production [5], and the steam reforming of naphtha is useful for hydrogen production, both for the chemical and petrochemical industry and as a clean fuel [6]. Hydrogen and syngas can also be produced starting from other different materials, such as methane [7], propane and polyethylene [8]. Catalytic naphtha reforming processes are diffused [9], but the use of catalysts can be problematic due to coke formation that causes their deactivation [10, 11]. Non-catalytic reactors can be used for syngas production through

the partial oxidation of hydrocarbons, and this kind of process has also been studied for heptane [12].

Starting from the above considerations, a broad experimental study on obtaining syngas from non-gaseous fuels in the temperature range 400-600°C is being developed, following the previous studies on a pyrolysis pilot plant and different biomass feeds [13, 14]; the economic advantages of this technology have already been discussed and demonstrated [15]. Working at such low temperatures presents both economic and operational advantages [16, 17].

Kinetic modeling is a powerful tool in the analysis of many reactant systems, and it has already been applied to gasification, pyrolysis, partial oxidation and combustion processes of hydrocarbon mixtures [18]. Detailed kinetic models have been developed for catalytic reforming [19, 20]. The development of appropriate kinetic models is also an essential component in the study of non-catalytic syngas production processes, in order to achieve the adequate information for design and scale-up purposes.

Heptane is one of the linear hydrocarbons, liquid at near to room temperature and with the smallest molecular weight; this is why it was chosen to begin our study and, at the same time, to test our experimental apparatus. To produce syngas, heptane can be partially oxidized [21]. Oxidation and pyrolysis of heptane are present in many scientific works [22], while the reaction between heptane and water has been studied by other researchers [23, 24]. This work presents experimental data for a simple approach to the kinetic modeling of the reaction between heptane and water for syngas production.

II. MATERIALS AND METHODS

A. Experimental Apparatus

The reactive process was conducted by means of a continuous heated stainless steel cylindrical reactor; its internal layout consisted of two chambers flushed in series, separated by a circular baffle (see Fig. 1) so as to achieve a nearly complete mixed fluid dynamic behaviour. The reactor was placed inside a muffle oven (ASAL s.r.l., model ZB1) and consequently heated and maintained at a constant temperature. The complete apparatus is schematically represented in Fig. 2.

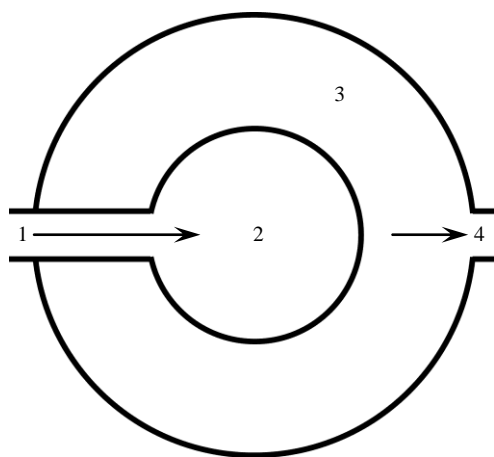


Figure 2. Scheme of the used reactor (1: inlet duct; 2: internal chamber; 3: external chamber; 4: outlet duct).

The liquid reactants, previously degassed by direct insufflation of pure helium into their reservoirs, were continuously fed to the reactor by a multichannel volumetric pump (Waters 600E) through a stainless steel tube (internal diameter: 1 mm) welded to the inlet of the reactor and passing through the door of the muffle. The pump allowed the reactor inlet volumetric liquid flow rate and the ratio of reagents to be regulated and changed.

The gaseous reaction products coming from the reactor exited the muffle in a stainless steel tube (internal diameter: 2.4 mm) passing through a hole at the back of the muffle. Next, they were quickly cooled at room temperature (about 25°C, to immediately stop the reactions) by means of immersing the tube in a water bath; the condensation of water and heavier (compounds with five or more carbon atoms) organic vapours was also obtained in the cooler.

Afterwards, a gas-liquid separator allowed the separation of the condensed liquids (water and organic phases) from the incondensable species (permanent gases and light hydrocarbons). Consequently, liquids were discharged, while the gas phase was sent to a chromatographic analysis system in

order to evaluate its composition. At this stage, the outlet liquid flow rate was measured by a precision balance (Ohaus®, model AV4102C) on which the collecting container was positioned, while the gas flow rate was measured by means of a digital flow meter (Agilent Technologies®, model ADM2000).

Gas composition analysis was performed by a DANI® GC1000 Gas Chromatograph (GC), equipped with two capillary columns, a PoraPLOT Q (Agilent Technologies®) and a Carboxen 1010 (Sigma-Aldrich®). The PoraPLOT Q column was 25 m long, with a 0.53 mm internal diameter PLOT fused-silica capillary column coated with a 20 µm thick film of styrene-divinylbenzene copolymer; the Carboxen 1010 column was 30 m long, with a 0.53 mm internal diameter PLOT fused-silica capillary column coated with a 50 µm thick carbon layer with a 7 Å pore diameter. The PoraPLOT column separated carbon dioxide, ethane and propane, whereas hydrogen, carbon monoxide, methane, nitrogen and oxygen were separated by the Carboxen column. To do this, the two columns were flushed in series with the analyte, and a timed pneumatic valve, positioned between the two columns, controlled the gas flux, sending the first species directly to the detector and the second ones to the Carboxen column.

The injector type was of the split/splitless type and operated in the split mode. Injection was automatically made from the gas flow by means of a pneumatic sampling valve switching its position at fixed times. As the sampling loop had a volume of 1 ml, the excess gas coming from the separator was discharged. The detector was of a TCD (Thermal Conductivity Detector) type.

During this work, helium (and nitrogen, if necessary, to better detect the hydrogen signals) was used as the carrier gas, while the following operative conditions were adopted: an injector and detector temperature of 150°C, column inlet pressure of 0.68 bar, temperature steps at 30°C (for 8.5 min), 150°C (for 32.7 min) and 220°C (for 10.0 min) with a heating rate of 50 K/min (total analysis time: 55.0 min); the Carboxen column was flushed for between 9.0 and 16.0 min. Data acquisition was provided by Clarity™ Chromatography Software (DataApex®), version 4.0.

B. Chemicals

The reagents used for all the experimental runs in this work

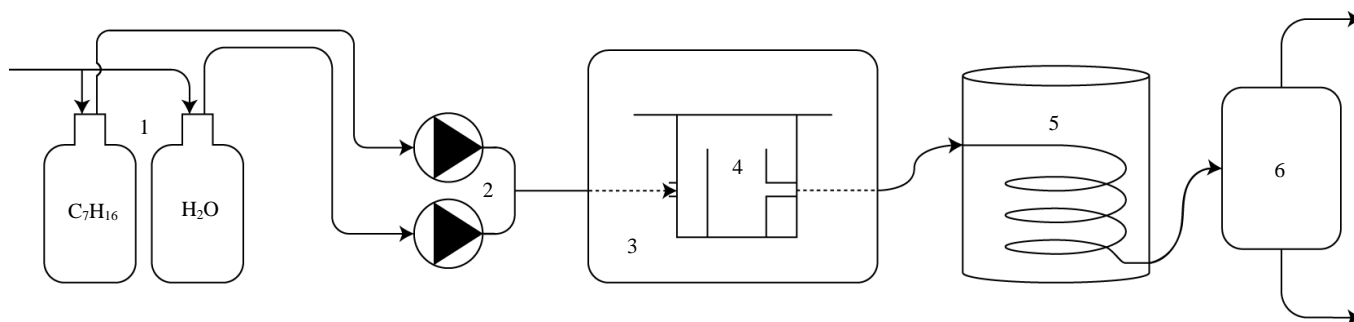


Figure 1. Scheme of the experimental apparatus (1: reagent reservoirs; 2: multichannel volumetric pump; 3: muffle oven; 4: reactor; 5: cooler-condenser; 6: phase separator).

were pure (99%) n-epthane (Carlo Erba®) and deionized water (produced in our laboratory).

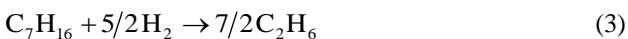
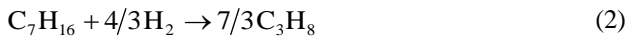
For the construction of the GC calibration curves, a particular standard gas mixture (SIAD®) was used. Standard components and their volumetric percentages were: hydrogen 45.30%, carbon monoxide 18.27%, carbon dioxide 13.32%, methane 9.39%, nitrogen 7.200%, ethane 1.950%, propane 3.530%, argon for the rest.

C. Kinetic Model

According to the literature [23], the first chemical reaction to be considered (assuming it to be irreversible) is the steam reforming of heptane:



Heptane is also subject to irreversible hydrocracking reactions giving propane, ethane and methane:



Then, four reversible reactions have to be considered, the first of which is the steam reforming of methane (the reverse of the methanation reaction):



The second reversible reaction involves carbon monoxide and water in the so-called “water gas shift” reaction:



Similarly to heptane, steam reforming reactions of ethane and propane were also taken into account:



The rate expressions of reactions from (1) to (8) in the homogeneous (gaseous) phase are the following, in the same order:

$$r_1 = k_1 P_{C_7H_{16}} P_{H_2O}^7 \quad (9)$$

$$r_2 = k_2 P_{C_7H_{16}} \frac{1}{7} P_{H_2}^{\frac{4}{21}} \quad (10)$$

$$r_3 = k_3 P_{C_7H_{16}} \frac{1}{7} P_{H_2}^{\frac{5}{14}} \quad (11)$$

$$r_4 = k_4 P_{C_7H_{16}} \frac{1}{7} P_{H_2}^{\frac{1}{2}} \quad (12)$$

$$r_5 = k_5 \left(P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_5} \right) \quad (13)$$

$$r_6 = k_6 \left(P_{CO} P_{H_2O} - \frac{P_{CO_2} P_{H_2}}{K_6} \right) \quad (14)$$

$$r_7 = k_7 \left(P_{C_2H_6} P_{H_2O}^2 - \frac{P_{H_2}^5 P_{CO}^2}{K_7} \right) \quad (15)$$

$$r_8 = k_8 \left(P_{C_3H_8} P_{H_2O}^3 - \frac{P_{H_2}^7 P_{CO}^3}{K_8} \right) \quad (16)$$

In Equations from (9) to (16), r_i represents the reaction rate of reaction i , k_i is the kinetic constant for reaction i , P_j indicates the partial pressure of the chemical component j and K_i is the equilibrium constant of reaction i . All the above reactions experimentally showed an elementary kinetic mechanism, with the sole exception of reaction (4), for which exponent 1/2 instead of 6/7 for P_{H_2} allowed much better adherence to the experimental data.

As already said, fluid dynamics in the reactor were assumed to be of perfect mixing (CSTR model). Thus, for each of the six main chemical species (hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and propane) detected by the GC analyses, a balance equation can be considered, as follows:

$$V = \frac{\dot{n}_{j,out} - \dot{n}_{j,in}}{R_j} \quad (17)$$

In Eq. (17) V is the volume of the reactor, $\dot{n}_{j,out}$ and $\dot{n}_{j,in}$ are, respectively, the outlet and inlet molar flow rate of component j , whereas R_j represents the generation rate for component j . With $\sigma_{i,j}$ indicating the stoichiometric coefficient of the chemical species j in the reaction i , and with N_R the number of reactions ($N_R = 8$ in this case), R_j is given by the following relationship:

$$R_j = \sum_{i=1}^{N_R} \sigma_{i,j} \cdot r_i \quad (18)$$

D. Experimental Operational Conditions

The kinetic constants for reactions from (1) to (8) were determined at the temperature of 500°C; this temperature was maintained constant by the thermostatisation system of the muffle oven; the total pressure was set at 1 atm. The following volumetric flow rates of feed were adopted: 0.10, 0.25, 0.35 and 1.25 cm³/min; the feed stream was constituted by 60% of heptane and 40% of water (volume percentages). The volume of the used reactor was 460 cm³.

III. RESULTS

The kinetic constants were numerically determined by the Ordinary Least Squares (OLS) method. The used values of the

equilibrium constants, calculated at the experimental temperature of 500°C by the group contribution method proposed in [25-27], are reported in Table I, whereas the

calculated kinetic constants for reactions from (1) to (8) are reported in Table II. Finally, in Fig. 3, the comparison between experimental compositions and those calculated by means of

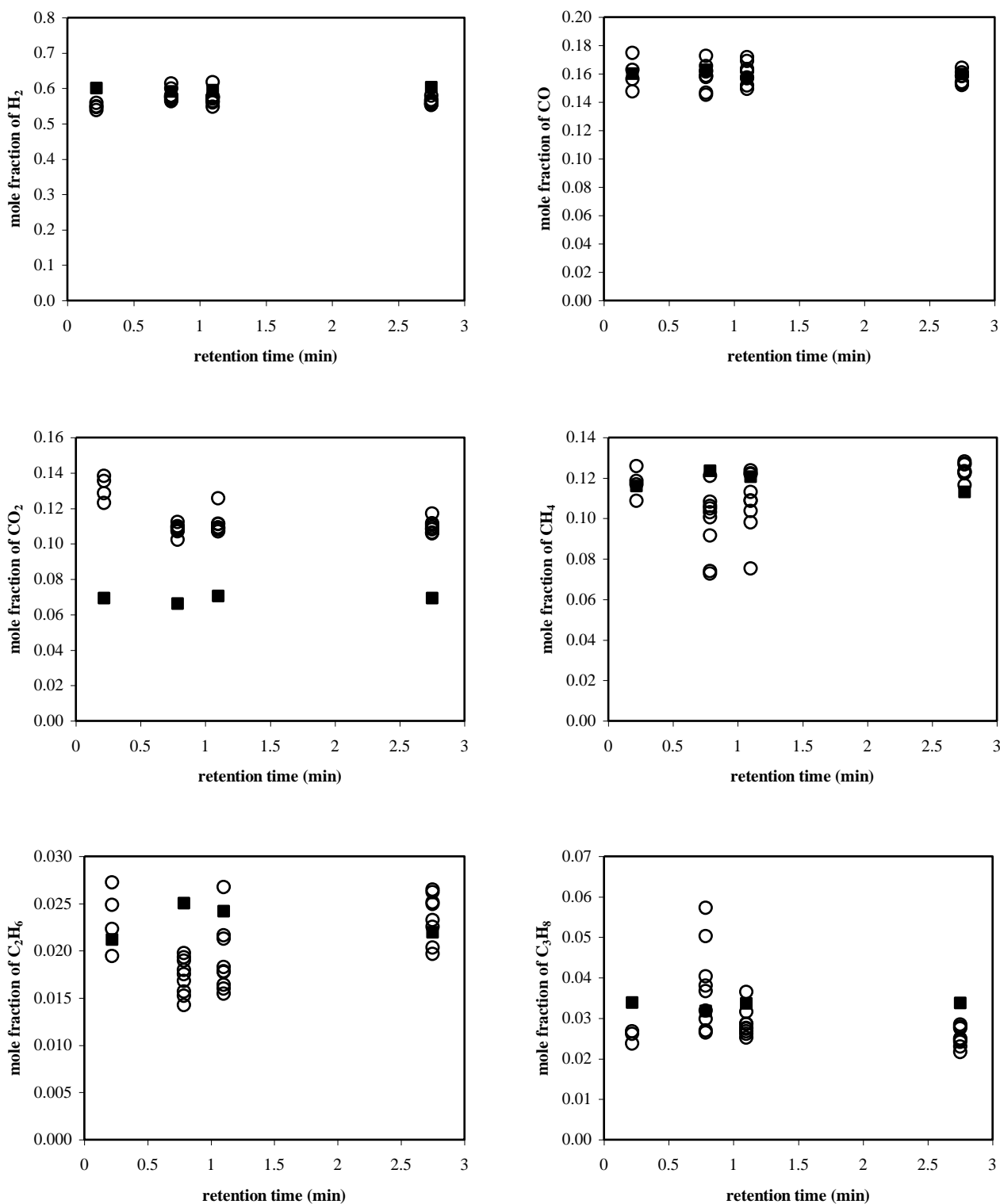


Figure 3. Experimental and model calculated mole fractions in the gas (incondensable) phase for hydrogen, carbon monoxide, carbon dioxide, methane, ethane and propane.

the model is shown.

IV. DISCUSSION AND CONCLUSIONS

As can be deduced from the data in Fig. 3, the developed kinetic model provides a good interpretation of the behavior of the considered reacting homogeneous system, and the assumption of complete mixing fluid dynamics was shown to be a good approximation. The only exception is the carbon dioxide concentration predicted by the model, as it is quite lower than the experimental values. The most likely reason for this marked deviation is that reaction (6) is the only one involving carbon dioxide, and this reaction could not be sufficient alone to justify the real production rate of this compound. The proposed kinetic model is probably lacking in one or more reactions producing carbon dioxide. A very likely reaction should be the complete combustion with oxygen (of mainly carbon monoxide but also of hydrocarbons), since the presence of free oxygen was not considered (it was not detected with the current GC analysis configuration). Even though the reagents were degassed by helium insufflation, this operation was probably far from completely eliminating the dissolved oxygen (and nitrogen), as the solubility in heptane is very high (the Ostwald coefficient for air solubility in n-heptane at 25°C is 0.245) [28]. In the future, a degassing

system made of membrane contactors operating in vacuum conditions will be used, and the presence of oxygen in the reagents will be carefully monitored.

The results of the present work will be extended with further studies on the influence of the reaction temperature and the reagent ratio; the range of pressure and residence time will also be extended. Subsequently, kinetic information will be integrated by feeding other hydrocarbons (pure and in mixtures) to the reactor. A good kinetic knowledge of such homogeneous reacting systems will be of great importance in the subsequent study of heterogeneous systems in the presence of solid biomass and with more complex fluid dynamics regimes.

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TABLE I. USED EQUILIBRIUM CONSTANTS

Reaction	Equilibrium Constant	
	Symbol	Numerical value ^a
5	K ₅	9.807·10 ¹
6	K ₆	5.275
7	K ₇	1.911·10 ⁸
8	K ₈	3.155·10 ¹⁴

a. Calculated by the methodology in [25-27] and referred to a reference pressure of 1 kPa.

TABLE II. FOUND KINETIC CONSTANTS

Reaction	Kinetic Constant		
	Symbol	Numerical value	Unit
1	k ₁	2.183·10 ⁻²⁰	mol/l/min/kPa ⁸
2	k ₂	5.289·10 ⁻⁵	mol/l/min/kPa ^(4/147)
3	k ₃	3.127·10 ⁻⁵	mol/l/min /kPa ^(5/98)
4	k ₄	8.899·10 ⁻⁵	mol/l/min /kPa ^(1/14)
5	k ₅	2.241·10 ⁻⁶	mol/l/min /kPa ²
6	k ₆	3.290·10 ⁻⁶	mol/l/min /kPa ²
7	k ₇	3.215·10 ⁻⁸	mol/l/min /kPa ³
8	k ₈	2.938·10 ⁻¹⁰	mol/l/min /kPa ⁴

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