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Kinetic Modelling of the Gas-Phase Water Oxidation of Light Hydrocarbons

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The conversion of solid and liquid fuels to gas, whenever possible, is an important way for improving the efficiency and cleanness of processes. This paper presents the kinetic modelling of the water oxidation of light hydrocarbons in the gas phase at 500 °C with mixtures of heptane and water in different amounts. The aim of the work was to find information about kinetics of the homogeneous chemical reactions which take place in the gas phase during the biomass processing, particularly pyrolysis, performed with water steam as the oxidizing reactant. The experimental data here used were obtained by a continuous stainless steel reactor placed inside a heated muffle oven and maintained at a constant temperature. The gaseous product, after separation of the condensable components, was analysed by an in-line gas chromatograph. The apparatus showed to be effective for future operations with different experimental conditions (temperature and feed). The obtained data will be integrated with those coming from parallel studies about the biomass wet pyrolysis for gas production.

1. Introduction

During the last decades many studies have been directed to the efficient use of carbon sources to obtain energy, also in the form of electricity (Chen et al., 2015), both on large and small scale. Many scientific works have been addressed to hydrogen production, through both traditional and innovative processes, like hydrogen sulphide splitting (Reverberi et al., 2016). Processing liquid fuels can present some technical and economic disadvantages, and even worse problems arise when solid fuels, such as biomass, are used without pre-treatment (Bridgwater et al., 2002). Sometimes it could be convenient to convert solid biomass to oil, and to process the latter, however this way can present the same problems occurring when processing liquid fuels (mainly the presence of contaminants). Gas production processes, such as co-gasification (Moghadam et al., 2014) or fast pyrolysis (Bridgwater et al., 2002), seem to be a promising way for obtaining electricity from biomass, since the possibility of previous cleaning. Among the possible gas production processes, great attention has also been devoted to hydro processing, e.g. in biofuel production (Furimsky, 2013), and to the steam reforming of naphtha (for hydrogen production), both for the chemical and petrochemical industry and as a clean fuel (Melo and Morlanés, 2005). Hydrogen and syngas can also be produced from other different organics, such as methane, propane and polyethylene (Gentillon and Toledo, 2013). Also catalytic reforming of naphtha is diffused (Rahimpour et al., 2013), but catalysts have high cost and can be problematic due to coke formation. On the contrary, non-catalytic reactors can be used for syngas production through the partial oxidation of hydrocarbons, and this kind of process has been studied for a lot of raw materials and fuels, like syngas from lignite and bituminous coal gasification (Thimthong et al., 2015) and from the pyrolysis of woody biomass (Ge et al., 2013), and also for heptane (Belmont et al., 2012).
Starting from the above considerations, at the moment a broad experimental activity on the topic of obtaining syngas from non-gaseous fuels is performed by the authors, particularly in the temperature range 400 - 600°C. The big effort is due to the technical and economic advantages of this kind of processes, which have already been discussed and demonstrated (Carta et al., 2012). In fact, working at such low temperatures surely presents both economic and operational advantages (Yang et al., 2011).
These studies need a proper kinetic modelling. Kinetic analyses have already been applied and described in the literature with respect to gasification, pyrolysis, partial oxidation and combustion of hydrocarbon mixtures

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(Ranzi et al., 2001); detailed kinetic models have also been developed for catalytic reforming (Wei et al., 2008). The development of appropriate kinetic models is also an essential part of the study of non-catalytic syngas production processes, in order to achieve the adequate information for design and scale-up purposes.
For the specific purpose above described, an experimental apparatus, better described in the next section, has been designed and realized. After this, the first tests were conducted with heptane and water. Heptane was chosen due to its properties: among the linear hydrocarbons, and liquid at room temperature, it has the smallest molecular weight. Furthermore, it can be partially oxidized to produce syngas (Al-Hamamre, 2013), and oxidation and pyrolysis of heptane can be found in many scientific works (Chaos et al., 2007); also the reaction involving heptane and water has been studied by other researchers, like Abashar (2013).
Thus, this work describes the experimental apparatus already mentioned and the first data which have been collected by operating with heptane and water for syngas production; finally, a simple approach to the kinetic modelling of the process is presented and discussed. The obtained data will be integrated with a parallel study by the authors about the wet pyrolysis of biomass for gas production, concerning both the fluid dynamic (Desogus and Carta, 2016a) and the kinetic (Desogus and Carta, 2016b) points of view.

2. Materials and methods

2.1 Experimental apparatus

The sketch of the experimental structure is shown in Figure 1a. The liquid reactants were degassed by direct insufflation of helium into their reservoirs, then they were continuously fed to the reactor, positioned inside a muffle oven, by a multichannel volumetric pump (Waters 600E) through a stainless steel tube (ID of 1 mm). Each flow rate could be regulated in such a way that also the ratio between the two could be changed.
The gaseous and vapour reaction products, coming from the reactor, exited the muffle through a stainless steel tube (internal diameter: 2.4 mm) by a hole at the back of the muffle. Next, the gas-vapour flow was quickly cooled at room temperature (about 25 °C) to immediately stop the reactions by a cold water bath in which the tube was immersed, in such a way that also the condensation of unreacted water and the heaviest (compounds with five or more carbon atoms) organic products could be obtained in the cooler.
Afterwards, the mixture (liquid and non-condensable gases) went to a gas-liquid separator in such a way that water and the organic liquid phase could be separated from the gas phase (permanent gases and light hydrocarbons). The collected liquids were discharged (they can eventually be withdrawn and analysed if necessary; this operation was not done during this work), while the gas phase was sent to a chromatographic analysis system in order to evaluate its composition. At this stage, to measure the outlet liquid flow rate, a technical balance (Ohaus®, model Adventurer™ Pro AV4102C) was used, recording the weight of the collecting container as a function of time; the balance was connected to a computer by an USB interface and the weight data were collected, at one second intervals, by the Ohaus® Data Acquisition Software. Finally, the gas flow rate was measured by means of a digital flow meter (Agilent Technologies®, model ADM2000).

2.2 Reaction equipment

The reactive process was conducted in a continuous heated stainless steel cylindrical reactor; its internal layout had two chambers flushed in series, separated by a circular baffle - Figures 1(b) and 1(c) so as to achieve a nearly complete mixed fluid dynamic behaviour. The reactor (Figure 1(d)) was placed inside a muffle oven (ASAL s.r.l., model ZB1, see Figure 1(e)), heated and maintained at a constant temperature.

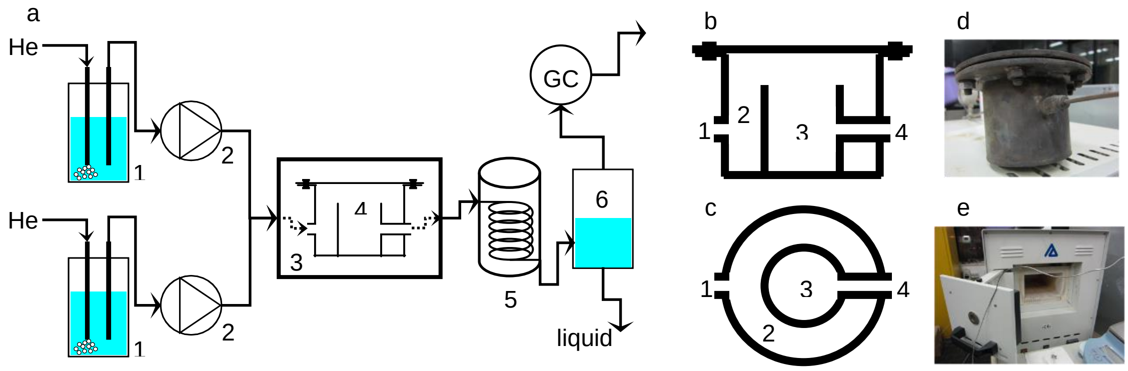

Figure 1: a) Experimental apparatus (1: reservoirs; 2: multichannel pump; 3: muffle oven; 4: reactor; 5: cooler-condenser; 6: phase separator; GC: gas chromatograph). Reaction equipment: b) vertical and c) horizontal section of the reactor, d) reactor, e) muffle oven; 1: inlet; 2: external chamber; 3: internal chamber; 4: outlet

2.3 Analysis equipment

Gas 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 first separated CO_2, C_2H_6 and C_3H_8, whereas H_2, CO, CH_4, N_2 and O_2 were separated by the second one. The two columns were flushed in series, and a timed pneumatic valve, positioned between the two columns, controlled the gas flux, sending the first species directly to the detector and the others to the Carboxen column.
The injector was operated in the split mode. Injection was made from the gas line by a timed pneumatic sampling valve switching at fixed times and filling the sampling loop (volume of 1 mL). The detector was a TCD (Thermal Conductivity Detector). Helium was the carrier, and this method was adopted: injector and TCD temperature of 150 °C, column inlet pressure of 0.68 bar, temperature steps at 30 °C (8.5 min), 150 °C (32.7 min) and 220 °C (10.0 min) with a heating rate of 50 K/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.

2.4 Chemicals

The reagents used for all the experimental runs in this work were pure (99 %) n-heptane (Carlo Erba®) and deionised 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: H_2 45.30 %, CO 18.27 %, CO_2 13.32 %, CH_4 9.39 %, N_2 7.200 %, C_2H_6 1.950 %, C_3H_8 3.530 %, Ar for the rest.

2.5 Kinetic modelling

The main reactions to be considered in the kinetic model were selected according to the literature information (Abashar, 2013). The first one is the steam reforming of heptane (assuming this reaction to be irreversible):

$$C_7H_{16} + 7\,H_2O \rightarrow 7\,CO + 15\,H_2 \tag*{3. (R1)}$$

In addition to (R1), C_7H_{16} is subject to irreversible hydro cracking reactions giving C_3H_8, C_2H_6 and CH_4:

$$C_7H_{16} + 4/3\,H_2 \rightarrow 7/3\,C_3H_8 \tag*{(R2)}$$

$$C_7H_{16} + 5/2\,H_2 \rightarrow 7/2\,C_2H_6 \tag*{(R3)}$$

$$C_7H_{16} + 6\,H_2 \rightarrow 7\,CH_4 \tag*{(R4)}$$

Then, four reversible reactions have to be considered, the first of which is the steam reforming of CH_4, and then the so-called "water gas shift" reaction and the steam reforming of C_2H_6 and C_3H_8:

$$CH_4 + H_2O \rightleftharpoons 3\,H_2 + CO \tag*{(R5)}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag*{(R6)}$$

$$C_2H_6 + 2\,H_2O \rightleftharpoons 5\,H_2 + 2\,CO \tag*{(R7)}$$

$$C_3H_8 + 3\,H_2O \rightleftharpoons 7\,H_2 + 3\,CO \tag*{(R8)}$$

Consequently, with the hypothesis of elementary reaction kinetic, the rate expressions of reactions from (R1) to (R8) in the homogeneous (gaseous) phase are the following, in the same order:

$$r_1 = k_1 P_{C_7H_{16}} P_{H_2O}{}^{7} \tag{1}$$

$$r_2 = k_2 P_{C_7H_{16}}{}^{1/7} P_{H_2}{}^{4/21} \tag{2}$$

$$r_3 = k_3 P_{C_7H_{16}}{}^{1/7} P_{H_2}{}^{5/14} \tag{3}$$

$$r_4 = k_4 P_{C_7H_{16}}{}^{1/7} P_{H_2}{}^{1/2} \tag{4}$$

$$r_5 = k_5 \left(P_{CH_4} P_{H_2O} - P_{H_2}{}^{3} P_{CO} \middle/ K_5 \right) \tag{5}$$

$$r_6 = k_6\left(P_{CO}P_{H_2O} - P_{CO_2}P_{H_2}/K_6\right) \tag{6}$$

$$r_7 = k_7\left(P_{C_2H_6}P_{H_2O}{}^{2} - P_{H_2}{}^{5}P_{CO}{}^{2}/K_7\right) \tag{7}$$

$$r_8 = k_8\left(P_{C_3H_8}P_{H_2O}{}^{3} - P_{H_2}{}^{7}P_{CO}{}^{3}/K_8\right) \tag{8}$$

In Eqs(1)-(8), r_i and k_i are the rate and the kinetic constant for reaction i, P_j is the partial pressure of the species j, and K_i is the equilibrium constant of reaction i. In effect, according to the initial hypothesis, all the above reactions experimentally showed an elementary kinetic mechanism, with the sole exception of reaction (R4), as in Eq(4) exponent 1/2 instead of 6/7 for P_{H_2} allowed a better adherence to the experimental data.

The fluid dynamics regime in the reactor was assumed to be of perfect mixing (CSTR model), like suggested by Fanti et al. (2015). Thus, for each of the six main chemical species which were considered (H_2, CO, CO_2, CH_4, C_2H_6, C_3H_8), and detected by the GC analyses, a balance equation can be considered, as follows:

$$V = \frac{\dot{n}_{j,out} - \dot{n}_{j,in}}{R_j} \tag{9}$$

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

$$R_j = \sum_{i=1}^{N_R} \sigma_{i,j} \cdot r_i \tag{10}$$

3.1 Experimental operational conditions

To test the reaction and analysis equipment and the kinetic model, experimental runs at the temperature of 500 °C were carried on in order to determine the kinetic constants for reactions from (R1) to (R8); the reaction temperature was maintained constant by the thermostatation system of the muffle oven, in which the stainless steel reactor was positioned; the total pressure was set at 1 atm. The following volumetric flow rates of reagent feed were adopted: 0.10, 0.25, 0.35 and 1.25 cm^3/min; the feed stream was constituted by 60 % of heptane and 40 % of water (volume percentages). The volume of the used reactor was 0.460 dm^3.

4. 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 by Van Krevelen and Chermin (1951), are reported in Table 1, whereas the calculated kinetic constants for reactions from (R1) to (R8) are reported in Table 2. Finally, in Figure 2, the comparison between experimental compositions and those calculated by means of the model is shown.

5. Discussion and conclusions

From the data in Figure 3, it can be deducted that the developed kinetic model provides a good description of the behaviour of the considered reacting homogeneous system, and the assumption of complete mixing fluid dynamics revealed to be sufficiently correct, probably with the only exception of the CO_2 concentration (Figure 3(c)) predicted by the model, considering that it is quite lower than the experimental values. The most likely reason for this deviation is that reaction (R6) is the only one taking into account CO_2, and this reaction could not be sufficient to justify the real production rate of this compound. The proposed kinetic model could be lacking in one or more reactions producing CO_2. 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), considering that the solubility of O_2 in C_7H_{16} is very high (as reported by Battino et al. (1984), the Ostwald coefficient for air solubility in C_7H_{16} at 25 °C is 0.245). In the future, a degassing system with membrane contactors operating in vacuum conditions will be used, hoping this system could be more efficient in eliminating the dissolved O_2, the presence of which among the reagents will be carefully monitored. The experimental apparatus here used showed to work well for the research purposes, thus 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. After this, the 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, as shown in parallel studies conducted by the same researchers (Desogus et al., 2016).

Table 1: Used equilibrium constants

	Equilibrium constant	
Reaction	Symbol	Numerical value*
(R5)	K_5	9.807×10^{1}
(R6)	K_6	5.275
(R7)	K_7	1.911×10^{8}
(R8)	K_8	3.155×10^{14}

*Calculated by the methodology of Van Krevelen and Chermin (1951) and referred to a pressure of 1 kPa.

Table 2: Calculated kinetic constants

	Kinetic constant		
Reaction	Symbol	Numerical value	Unit
(R1)	k_1	2.183×10^{-20}	$mol/(dm^3 \cdot min \cdot kPa^8)$
(R2)	k_2	$5.289 \cdot \times 10^{-5}$	$mol/(dm^3 \cdot min \cdot kPa^{(4/147)})$
(R3)	k_3	3.127×10^{-5}	$mol/(dm^3 \cdot min \cdot kPa^{(5/98)})$
(R4)	k_4	8.899×10^{-5}	$mol/(dm^3 \cdot min \cdot kPa^{(1/14)})$
(R5)	k_5	2.241×10^{-6}	$mol/(dm^3 \cdot min \cdot kPa^2)$
(R6)	k_6	3.290×10^{-6}	$mol/(dm^3 \cdot min \cdot kPa^2)$
(R7)	k_7	3.215×10^{-8}	$mol/(dm^3 \cdot min \cdot kPa^3)$
(R8)	k_8	2.938×10^{-10}	$mol/(dm^3 \cdot min \cdot kPa^4)$

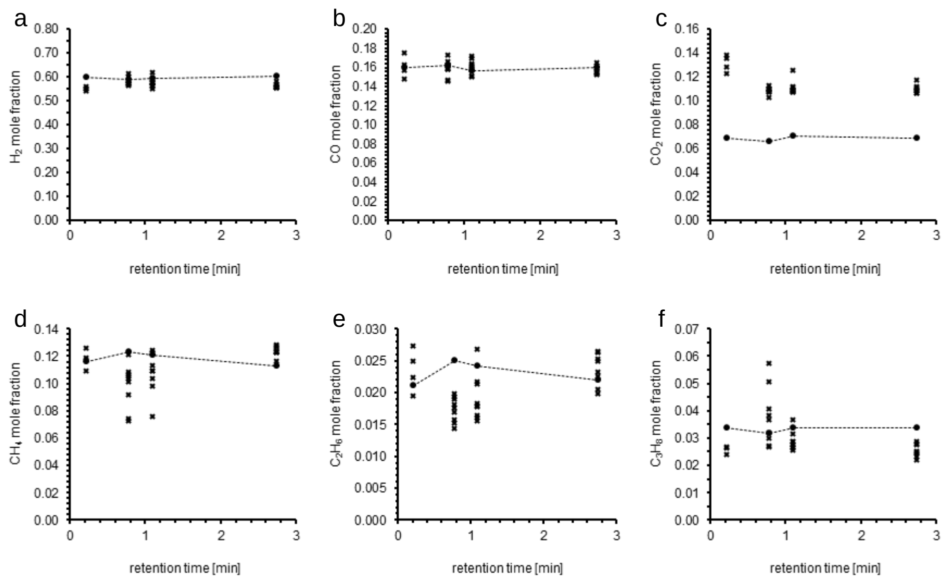

Figure 2: Experimental (×) and model calculated (●) mole fractions in the gas (incondensable) phase as a function of the retention time for: a) H_2, b) CO, c) CO_2, d) CH_4, e) C_2H_6, f) C_3H_8.

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