

GHGT-12

Effect of the injection of a gas mixture (CO<sub>2</sub> + O<sub>2</sub>) onto residual hydrocarbons in a depleted oil reservoir: experiments and modelling

Claire PACINI<sup>a</sup>, Pranay MORAJKAR<sup>b</sup>, Pierre FAURE<sup>c</sup>, Valérie BURKLE-VITZTHUM<sup>d</sup>, Aurélien RANDI<sup>a</sup>, Catherine LORGEOUX<sup>a</sup>, Jacques PIRONON<sup>a\*</sup>,  
Danielle MOREL<sup>e</sup>

<sup>a</sup> Université de Lorraine, CNRS, CREGU, GeoRessources laboratory, BP 70239, Vandœuvre-lès-Nancy, F-54506, France

<sup>b</sup> Goa University, Department Of Chemistry, Taleigao Plateau-403206, Goa, India

<sup>c</sup> Université de Lorraine, CNRS, CREGU, LIEC laboratory, Vandœuvre-lès-Nancy, F-54500, France

<sup>d</sup> Université de Lorraine, CNRS, LRGP laboratory, F-54001, Nancy, France

<sup>e</sup> TOTAL, CSTJF, F-64018, Pau, France

---

**Abstract**

CO<sub>2</sub> geo-sequestration in hydrocarbon reservoirs is suggested as solution for limiting CO<sub>2</sub> atmospheric accumulation. In the case of oxy-combustion CO<sub>2</sub> capture, the main annex gas associated with CO<sub>2</sub> is O<sub>2</sub> in important proportion. To predict the hydrocarbon evolution in the presence of O<sub>2</sub> in oil-depleted reservoir, it is essential to investigate their reactivity by a double approach combining experimentation and modelling.

Experiments were carried out on a model compound (*n*-octane) and a detailed kinetic model for *n*-octane was applied. The consistency between experimentations and model is promising for the development of a tool allowing the prediction of hydrocarbon reservoir stability.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of the Organizing Committee of GHGT-12

*Keywords:* oxy-combustion; oil depleted reservoir, experiments, chemical modelling, CO<sub>2</sub> + O<sub>2</sub> mixture, oxidation, *n*-octane

---

---

\* Corresponding author. Tel.: +33 3 83 68 47 32; fax: +33 3 83 68 47 01.

*E-mail address:* [jacques.pironon@univ-lorraine.fr](mailto:jacques.pironon@univ-lorraine.fr)

## 1. Introduction

It is now accepted that the combustion of fossil organic matter is partly responsible for the increase in atmospheric concentrations of carbon dioxide. In addition, it is considered that this increase contributes to global warming of the Earth.

CO<sub>2</sub> geological storage (CCS, i.e. CO<sub>2</sub> Capture and Storage) is considered as an interesting option to reduce the emission of this major greenhouse gas [1]. CO<sub>2</sub> geo-sequestration consists of the following steps: (i) CO<sub>2</sub> capture at the industrial source, (ii) transportation from the source to the storage location mainly by pipeline, and (iii) long-term storage in deep geological reservoir [2]. CO<sub>2</sub> can be captured from major CO<sub>2</sub> emitting industries like natural gas production, synthetic or fossil fuel plants. A power plant with CCS could reduce CO<sub>2</sub> atmospheric emissions by approximately 80-90 % compared to a plant without CCS [1]. There are different types of capture processes: (i) pre-combustion, (ii) post-combustion and (iii) oxy-combustion. Oxy-combustion capture process (combustion in high oxygen concentration = 90-95 %) provides a better combustion efficiency than the other combustions, and leads to CO<sub>2</sub> enriched gas stream. Indeed, oxy-combustion limits the production of nitrogenated gases (especially NO<sub>x</sub> and N<sub>2</sub>O). But relatively high levels of impurities can remain in the gas stream, like water, Ar (0-5%), N<sub>2</sub> (0-15%), O<sub>2</sub> (0-7%), SO<sub>2</sub> (0 1.5%) [3].

Water is generally removed from gas mixture by condensation. But it is not planned to achieve a complete CO<sub>2</sub> separation from the other annex gases, because of (i) the high cost of the purification steps, (ii) the increase in the energy penalty and (iii) the reduced CO<sub>2</sub> avoidance [4].

Impurities could greatly affect the thermodynamic properties of the gas stream, which in turn would affect the different steps of CCS process. Few studies have examined the impacts of annex gases co-injected with CO<sub>2</sub> on hydrocarbons remaining in oil and gas reservoirs. Especially, the injection of O<sub>2</sub> associated with CO<sub>2</sub> after oxy-combustion capture processes can induce oxidation of hydrocarbons contained in oil reservoirs, until auto-ignition. Even if hydrocarbon oxidation processes by O<sub>2</sub> are well known in high-temperature - low-pressure (HT-LP, 500 to 900 K, < 1 MPa) conditions, scarce data are available under reservoir conditions (high-pressure - low-temperature, HP-LT, < 473 K, 1 to 100 MPa).

Hence, it is extremely important to investigate the reactivity of hydrocarbons towards O<sub>2</sub> under reservoir conditions for CCS to establish what could be the evolution of fluids in the reservoir.

In this study we intend to investigate the O<sub>2</sub> initiated oxidation chemistry of *n*-octane (*n*-C<sub>8</sub>H<sub>18</sub>) as a model compound in context of CO<sub>2</sub>/O<sub>2</sub> injection in oil reservoir, under low temperature and high pressure, in order to study the geo-sequestration of CO<sub>2</sub>. Experiments and simulations using detailed kinetic models have been performed in parallel to explain the reactivity of *n*-C<sub>8</sub>H<sub>18</sub> in presence of O<sub>2</sub> under reservoir conditions.

## 2. Materials and methods

### 2.1. Experiment

Oxidation experimentations were carried out with an original single experimental device developed in the lab. This device is composed of two parts (i) an experimental and (ii) an analytical part. A schematic representation of the experimental setup is shown in Figure 1.

To be close to the reservoir conditions, oxidation experiments were carried out in a high pressure/low temperature reactor. The system was isochoric (volume: 500 ml) and isothermal. In the reactor, an electromagnetic propeller stirrer allowed a homogenization of the content. The titanium reactor was placed in an oven, whose temperature could be varied up to 448 K.

The reactor was connected with a Rolsi® valve (Rapid On-Line Sampler Injector). The Rolsi® valve is a gas sampling valve which allowed on-line micro-sampling (from 0.01 mg to 10 mg), and so a continuous monitoring of the system during the time of the experiment. The Rolsi® valve was connected to a transfer line, which was heated at the reactor temperature, under 0.05 MPa of argon. The transfer line allowed the sample circulation from the experimental part to the analytical part.

Sample analyses were carried out with a gas micro-chromatogram SRA R-3000 ( $\mu$ -GC), coupled with three modules. Each module included (i) a pressure regulator, (ii) a tyre and wheel assembly of injection micro-valve, (iii) an injection valve, (iv) a capillary column and (v) a Thermal Conductivity Detector (TCD).

The  $\mu$ -GC allowed analysis of the following gas compounds:

- 1st module: He, N<sub>2</sub>, O<sub>2</sub>, CO, CH<sub>4</sub>
- 2nd module: CO<sub>2</sub>
- 3rd module: H<sub>2</sub>O, *n*-C<sub>8</sub>H<sub>18</sub>

Standard gases were used as reference to calibrate the different gas compounds (N<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O) and a solution of pure *n*-C<sub>8</sub>H<sub>18</sub> was injected at different concentrations to construct a calibration plot for the reactant.

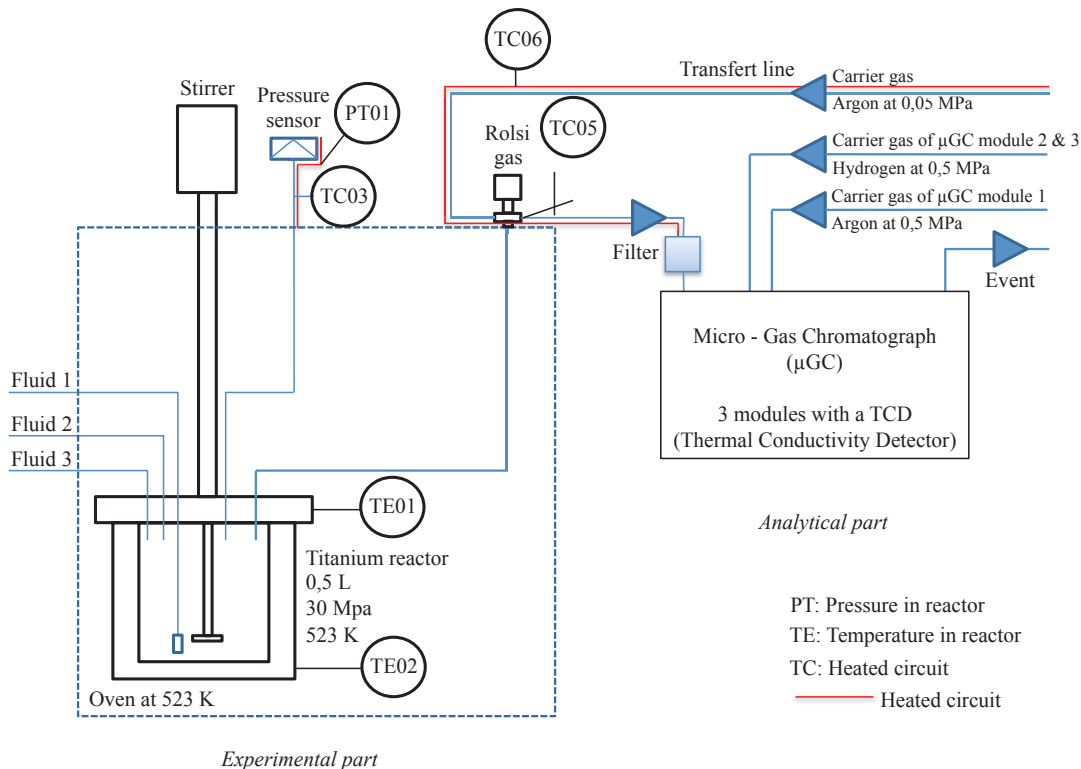


Fig. 1. Experimental device with the detail of the Experimental and Analytical parts

Three experiments were carried out with *n*-C<sub>8</sub>H<sub>18</sub> in the presence of 20 % O<sub>2</sub> and 80 % N<sub>2</sub> (artificial air), at 398 K, 423 K, 448 K, each at 20 MPa, to investigate the effect of initial temperature on the oxidation kinetics. Moreover, another experiment was carried out with *n*-C<sub>8</sub>H<sub>18</sub> in the presence of 3 % O<sub>2</sub> and 97 % N<sub>2</sub> at 423 K and 20 MPa, to investigate the effect of O<sub>2</sub> concentration on the oxidation kinetics (Table 1). Gas solvent was tested in a previous study; we showed that nitrogen and carbon dioxide had no influence on the oxidation kinetic and reactivity. Hence, nitrogen was selected such as gas solvent rather than CO<sub>2</sub>, to be able to quantify CO<sub>2</sub> production during oxidation.

The reactant (approximately 1 g of *n*-C<sub>8</sub>H<sub>18</sub>) was placed in the reactor at atmospheric temperature and pressure. The reactor was purged with helium to eliminate the residual air from the reactor, followed by addition of 0.2 MPa He, as internal standard.

Gas mixtures were injected into the reactor at ambient temperature. The reactor was heated up to 398, 423 or 448 K and by consequence, the pressure attained 20 MPa after stabilization of the temperature. The temperature was measured by a calibrated thermocouple and the pressure by a pressure sensor during all the experiment.

Table 1. Mole fraction reactants, temperature and pressure applied for closed experiments during 48 hours.

<i>n</i> -octane (mole fraction)	O <sub>2</sub> (mole fraction)	N <sub>2</sub> (mole fraction)	Temperature (K)	Pressure (MPa)
0.29	19.94	79.77	398	20
0.31	19.94	79.75	423	20
0.31	2.99	96.70	423	20
0.33	19.93	79.74	448	20

## 2.2. Modelling

A detailed kinetic model for the oxidation of *n*-C<sub>8</sub>H<sub>18</sub> was generated using the software EXGAS [5]. EXGAS is a computer package developed to perform the automatic generation of detailed kinetic models for the gas-phase oxidation and pyrolysis of linear and branched alkanes or alkenes. As this package and its application to model the oxidation or pyrolysis of a wide range of alkanes have been already described, the general features of EXGAS will not be described here [6].

The thermo-chemical data are automatically calculated for molecules and radicals using the software THERGAS [7] based on the group and bond additivity methods proposed by Benson [8] and stored as 14 polynomial coefficients, according to CHEMKIN formalism [9]. The kinetic parameters were generated using the software KINGAS [10]. Kinetic modelling was performed with CHEMKIN II using the code SENKIN [11] for the simulation in closed isochoric reactor; the thermal output was fixed to allow simulating an adiabatic or an isothermal reactor. In order to explain the experimental results, the initial model was modified either by adjusting the kinetic parameters wherever applicable (within the uncertainties) or by adding the missing reactions that were not accounted for by EXGAS. The modified model comprises 3760 reactions and 394 species.

## 3. Results and discussions

The concentration of *n*-C<sub>8</sub>H<sub>18</sub> as a function of reaction time was monitored throughout the oxidation experiment. Fig. 2 and 3 present the experimental results of oxidation kinetics of *n*-C<sub>8</sub>H<sub>18</sub> mole fraction normalized by the initial mole fraction versus time (decay kinetics of *n*-C<sub>8</sub>H<sub>18</sub>), obtained from a series of experiments conducted at the above mentioned temperatures and from corresponding simulations.

### 3.1. Experiments

The temperature remained constant throughout all experiments with 3 % and 20 % of O<sub>2</sub> at 398, 423 and 448 K, which confirms the isothermal conditions of our experiments. A similar observation was made for the pressure, which was maintained at 20 MPa during all experiments.

The decay kinetics of *n*-C<sub>8</sub>H<sub>18</sub> at 423 and 448 K increased rapidly after a short delay of < 3 hours, which then subsided into a slower kinetic until all *n*-C<sub>8</sub>H<sub>18</sub> was consumed (~ 50 hours at 448 K). The experiment at 423 K showed very slow consumption kinetics of *n*-C<sub>8</sub>H<sub>18</sub>.

The kinetics at 398 K was the slowest one and only 25 % conversion of *n*-C<sub>8</sub>H<sub>18</sub> after 48 hours was achieved. The rate of conversion increased with the temperature, leading to 70 % and 96 % conversion of the initial carbon content after 48 hours at 423 and 448 K respectively (fig. 2).

The conversion rate of the *n*-C<sub>8</sub>H<sub>18</sub> for the experiments with 3 % and 20 % of O<sub>2</sub> had a similar evolution, with a rapid increase at the beginning of the experiments and a kinetic decrease after 40 hours (fig. 3).

### 3.2. Modelling

To simulate the observed decay kinetics of  $n\text{-C}_8\text{H}_{18}$ , a detailed kinetic model was constructed using EXGAS. Kinetic modelling was performed using the reaction mechanism along with the initial experimental parameters such as concentration, temperature and pressure and the results of the simulation were compared with the experimental results of  $n\text{-C}_8\text{H}_{18}$  concentration evolution.

Numerical results are in good accordance with experimental data. The global trends between modelling and experimental oxidations are similar as the oxidation kinetics. The modified model simulating the oxidation kinetics of  $n\text{-C}_8\text{H}_{18}$  under reservoir conditions (HP – LT) was validated by comparison between the experimental observations and the simulation results at three different reaction temperatures (fig. 2) and two different  $\text{O}_2$  concentrations (fig. 3).

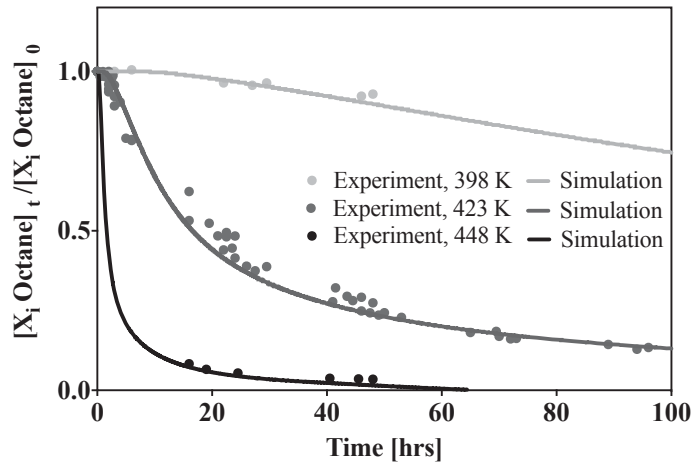


Fig. 2. Decay kinetics of  $n\text{-C}_8\text{H}_{18}$  versus time for experiment and modelling at three temperatures.

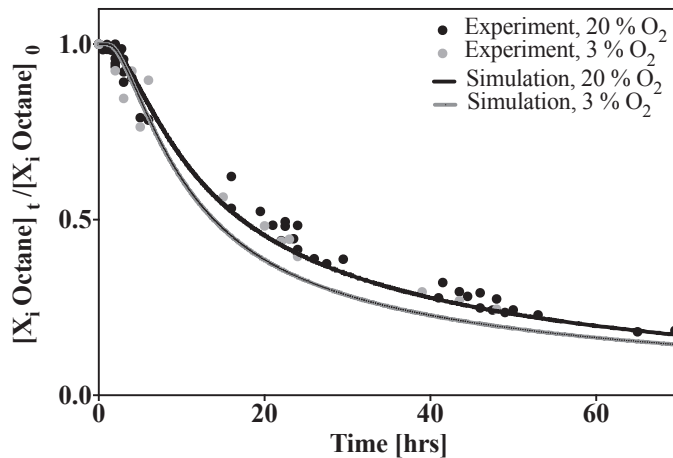


Fig. 3. Decay kinetics of  $n\text{-C}_8\text{H}_{18}$  versus time for experiment and modelling for two  $\text{O}_2$  contents.

#### 4. Conclusions

This is the first experimental study of oxidation kinetics of  $n\text{-C}_8\text{H}_{18}$  under reservoir conditions, i.e, low temperature and high pressure. In the original device developed for this study, auto-ignition was never reached in the studied conditions. Nevertheless, the oxidation kinetics is rather fast since 96% conversion of the initial carbon content was reached after 48 h at 448 K. A detailed kinetic model has been constructed and used to simulate the oxidation kinetics of  $n\text{-C}_8\text{H}_{18}$ , with the improvement of the primary mechanism of EXGAS model. The modified model was validated by comparison between the experimental observations at three different reaction temperatures and two different  $\text{O}_2$  concentrations, and the simulation results. The good agreement between our experiments and our improved numerical model is promising for the development of a tool for the prediction of stability of hydrocarbon reservoirs in CCS context. For now, the study was conducted in isothermal conditions. The next step will be to take into account the heat transfer properties of the reservoirs in order to evaluate the auto-ignition risk in conditions close to real ones.

#### Acknowledgements

This work has been supported by Chaire industrielle « CAPTAGE, TRANSPORT ET STOCKAGE DU  $\text{CO}_2$  » of Mines Paris Tech and TOTAL.

#### References

- [1] Metz, B., Davidson, O., de Coninck, H. C., Loos, M. and Meyer, L. A. (2005). *Ippc Special Report on Carbon Dioxide Capture and Storage*, Prepared by Working Group Iii of the Ippc. New York, Cambridge University Press: 442.
- [2] Kaldi, J. G., Gibson-Poole, C. M. and Payenberg, T. H. D. (2009). Geological Input to Selection and Evaluation of  $\text{CO}_2$  Geosequestration Sites. *Carbon Dioxide sequestration in geological media - State of the science : AAPG Studies in Geology 59*: p. 5 - 16.
- [3] Li, H., Yan, J. and Anheden, M. (2009). Impurity Impacts on the Purification Process in Oxy-Fuel Combustion Based  $\text{CO}_2$  Capture and Storage System. *Applied Energy 86(2)*: 202-213.
- [4] Mikunda, T. (2012).  $\text{CO}_2$  Storage: Do Impurities Matter? *Carbon Capture Journal*.
- [5] Battin-Leclerc, F., Biet, J., Bounaceur, R., Côme, G. M., Fournet, R., Glaude, P.-A., Grandmougin, X., Herbinet, O., Scacchi, G. and Warth, V. (2010). *Exgas-Alkanes-Esters : A Software for the Automatic Generation of Mechanisms for the Oxidation of Alkanes and Esters*. LRGF, UPR CNRS 3349.
- [6] Dahm, K. D., Virk, P. S., Bounaceur, R., Battin-Leclerc, F., Marquaire, P. M., Fournet, R., Daniau, E. and Bouchez, M. (2004). Experimental and Modelling Investigation of the Thermal Decomposition of *N*-Dodecane. *Journal of Analytical and Applied Pyrolysis 71(2)*: 865-881.
- [7] Muller, C., Michel, V., Scacchi, G. and Come, G. M. (1995). *Thergas: A Computer Program for the Evaluation of Thermochemical Data of Molecules and Free Radicals in the Gas Phase*. *Journal de Chimie Physique et de Physico-Chimie Biologique 92(5)*: 1154-1178
- [8] Benson, S. W. (1976). *Thermochemical Kinetics*.
- [9] Kee, R. J., Rupley, F. M. and Miller, J. A. (1995). *Chemkin II : A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics*. Sandia Report.
- [10] Bloch-Michel, V. and Scacchi, G. (1995). *Estimation of Kinetic Parameters of Gas Phase Elementary Processes*, PhD.
- [11] Lutz, A. E., Kee, R. J. and Miller, J. A. (1995). *Senkin : A Fortran Program for Predicting Homogenous Gas-Phase Chemical Kinetics with Sensitivity Analysis* Sandia Report.