

## **Effect of pressure on the gasification of dodecane with steam and supercritical water and consequences on H<sub>2</sub> production**

Ana M. Sanchez-Hernandez,<sup>a</sup> Nicolas Martin-Sanchez,<sup>a</sup> M. Jesus Sanchez-Montero,<sup>a</sup>  
Carmen Izquierdo,<sup>a</sup> Francisco Salvador<sup>a,\*</sup>

*<sup>a</sup>Dpto. Química Física. Facultad de Ciencias Químicas. Universidad de Salamanca. Plaza  
de la Merced s/n 37008 Salamanca. Spain.*

### **E-mail addresses:**

Ana M. Sanchez-Hernandez: [anamsh@usal.es](mailto:anamsh@usal.es)

Nicolas Martin-Sanchez: [nicolas\\_martin@usal.es](mailto:nicolas_martin@usal.es)

M. Jesus Sanchez-Montero: [chusan@usal.es](mailto:chusan@usal.es)

Carmen Izquierdo: [misiego@usal.es](mailto:misiego@usal.es)

Francisco Salvador: [salvador@usal.es](mailto:salvador@usal.es)

### **\* Corresponding Author:**

Prof. Francisco Salvador Palacios. Phone: +34 677549970. E-mail: [salvador@usal.es](mailto:salvador@usal.es)

### S1) GC–MS analysis of liquid samples

The liquid samples were analyzed by gas chromatography with mass spectrometry (GC–MS) on an Agilent 7890a chromatograph equipped with an MS detector with an ionic trap Agilent MS220. A homogeneous 1  $\mu\text{L}$  sample was extracted with 1 mL of ethyl acetate. Then, 1  $\mu\text{L}$  of the extract was injected in the chromatograph with a split ratio 20:1. An Agilent VF-5 chromatographic column was used, with a length of 30 m; an internal diameter of 0.25 mm; and a thick layer of 25 micron, with 25 mL/min of He as the carrier gas. The injector was maintained at 270  $^{\circ}\text{C}$ , and the following temperature program was used in the oven: an initial temperature of 50  $^{\circ}\text{C}$  maintained for 5 min, followed by heating at 10  $^{\circ}\text{C}/\text{min}$  to 270  $^{\circ}\text{C}$ , which was finally maintained for 5 min. The detection mode was selected as electronic impact ionization. Masses from 50 to 500 uma were recorded.

### S2) Effect of the Gibbs free energy, $\Delta G^0$ , on the equilibrium constant

The equilibrium constant,  $K$ , at a reaction temperature  $T$  can be expressed as follows, eqn.

(S1):

$$K(T) = \exp\left[-\frac{\Delta G^0(T)}{RT}\right] \quad (\text{S1})$$

$\Delta G^0$  is defined by eqn. (S2):

$$\Delta G^0(T) = \Delta H^0(T) - T \cdot \Delta S^0(T) \quad (\text{S2})$$

Where  $\Delta H^0$  and  $\Delta S^0$  are the standard reaction enthalpy and entropy, respectively. On the other hand,  $K(T)$  could be expressed as follows, eqn (S3):

$$K(T) = K_0 \cdot K_1 \cdot K_2 \quad (\text{S3})$$

$K_0$ , eqn (S4), represents the equilibrium constant at the reference temperature,  $T_0 = 25\text{ }^\circ\text{C}$ , hence it does not depend on temperature.

$$K_0 = \exp\left[-\frac{\Delta G^0(T_0)}{RT_0}\right] \quad (\text{S4})$$

$K_1$ , eqn (S5), provides the main effect of temperature. Namely, the product ( $K_0 \cdot K_1$ ) is considered as the equilibrium constant at T when the reaction heat is considered as non-depending on temperature.

$$K_1 = \exp\left\{\left[\frac{\Delta H^0(T_0)}{RT_0}\right] \cdot \left(1 - \frac{T_0}{T}\right)\right\} \quad (\text{S5})$$

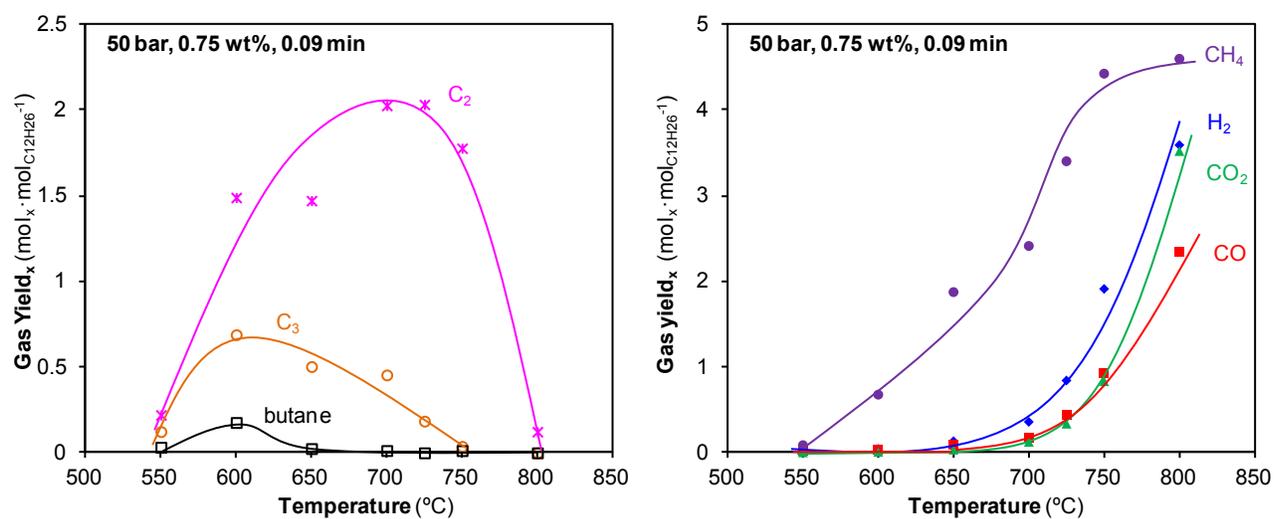
$K_2$ , eqn (S6), provides the little effect of temperature on K as a consequence of the changes in  $\Delta H^0$  and  $\Delta S^0$  with temperature.

$$K_2 = \exp\left\{-\left(\frac{1}{T}\right) \cdot \int_{T_0}^T \left(\frac{\Delta C_p^0}{R} \cdot dT\right) \cdot \int_{T_0}^T \left(\frac{\Delta C_p^0}{R} \cdot \frac{dT}{T}\right)\right\} \quad (\text{S6})$$

Consequently, the increase of reaction temperature in endothermic reactions ( $\Delta H^0 > 0$ ) makes  $K_1$  and K increase, thus leading to greater conversions.

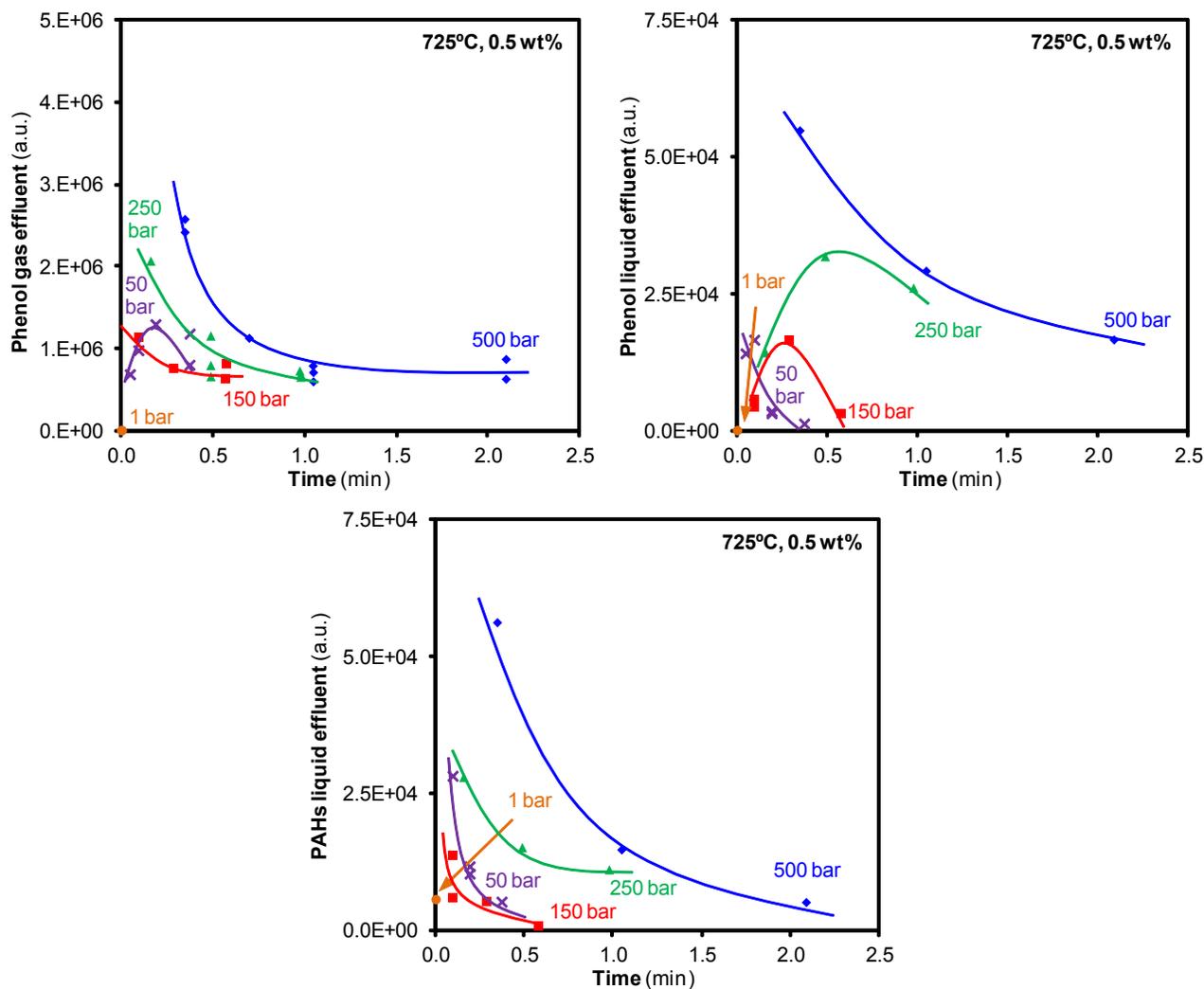
### S3) Effect of temperature on the gas yields of the species contained in the gaseous

effluent



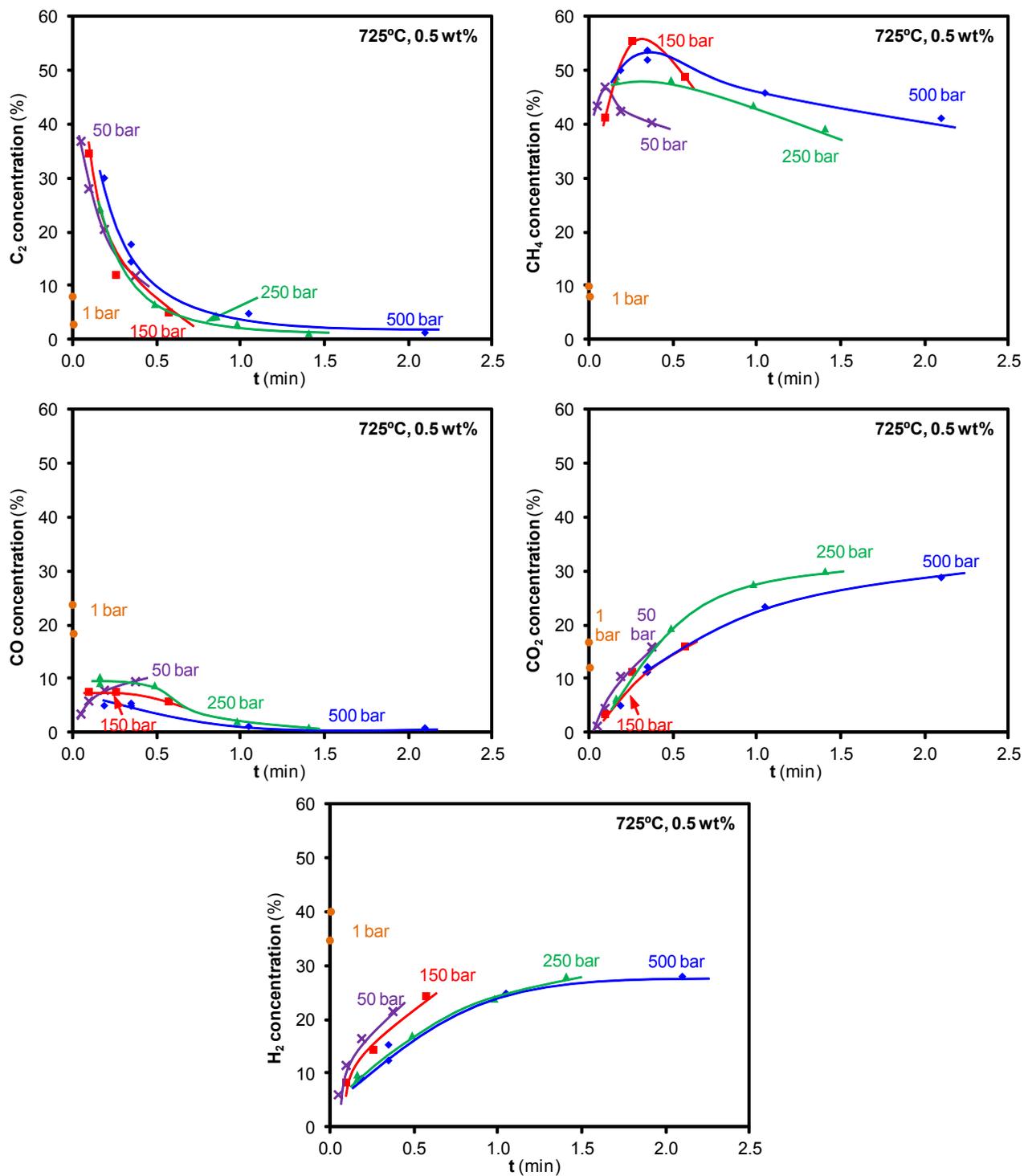
**Fig S1** Effect of temperature on the gas yields of the species contained in the gaseous effluent.

**S4) Effect of pressure and reaction time on the amounts of phenol and PAHs contained in the liquid and gaseous effluents (725°C)**



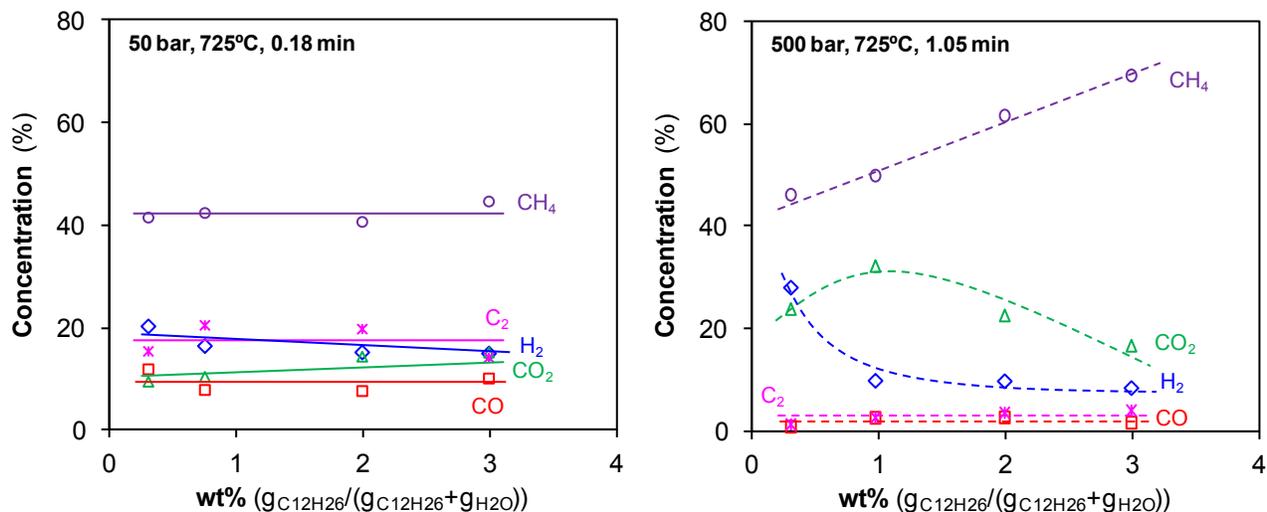
**Fig S2** Effect of pressure and reaction time on the amounts of phenol and PAHs contained in the liquid and gaseous effluents (725°C).

**S5) Effect of pressure and reaction time on the concentrations of the species contained in the gaseous effluent (725°C)**



**Fig S3** Effect of pressure and reaction time on the concentrations of the species contained in the gaseous effluent (725°C).

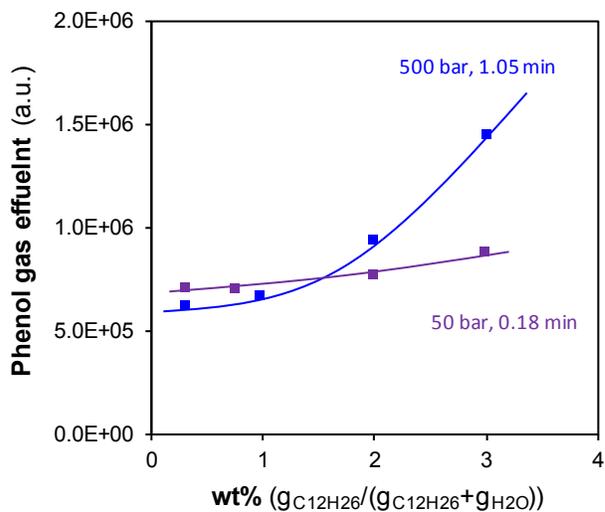
**S6) Effect of wt% on the concentration of the species contained in the gaseous effluents generated at 725°C under different pressure and reaction time conditions**



**Fig S4** Effect of wt% on the concentration of the species contained in the gaseous effluents generated at 725°C under different pressure and reaction time conditions.

CGE of gasification at 50 bar for 0.18 min hardly varies with wt%. Consequently, the concentrations of the gases hardly change with wt%; H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub> concentrations keep about 17.0, 10.0, 13.0, 42.5, and 17.5%, respectively. CGE clearly decreases with wt% in gasification at 500 bar for 1.05 min. For these experiments, CO<sub>2</sub> and H<sub>2</sub> concentrations decrease with wt% whereas CH<sub>4</sub> concentration increases; CO and C<sub>2</sub> concentrations are essentially equal to zero in the whole range assayed.

**S7) Effect of wt% on the amount of phenol contained in the gaseous effluents generated at 725°C under different pressure and reaction time conditions**



**Fig S5** Effect of wt% on the amount of phenol contained in the gaseous effluents generated at 725°C under different pressure and reaction time conditions.