Conversion of a resistant pollutant, phenol, into green fuels by gasification using supercritical water compressed up to 1000 bar

Nicolas Martin-Sanchez,[a] M. Jesus Sanchez-Montero,[a] Carmen Izquierdo,[a] Francisco Salvador [a,*]

[a]Dpto. Química Física. Facultad de Ciencias Químicas. Universidad de Salamanca. Plaza de la Merced s/n 37008 Salamanca. Spain.

E-mail addresses:

Nicolas Martin-Sanchez: nicolas_martin@usal.es

M. Jesus Sanchez-Montero: chusan@usal.es

Carmen Izquierdo: misiego@usal.es

Francisco Salvador: salvador@usal.es

* Corresponding Author:

Prof. Francisco Salvador Palacios. Phone: +34 677549970. E-mail: salvador@usal.es

SUPPLEMENTARY INFORMATION

S1) Mechanistic pathways for the phenol–water reaction identified in bibliography

The study by Professor Savage's group[1-4] revealed that phenol participates in several pathways for the formation of gaseous products. It can (i) be directly converted into the so-called "gasifiable products", which are intermediate species serving as the precursor of the final gasification, (ii) decompose to form benzene, or (iii) couple to form other compounds, such as dibenzofuran, before undergoing further decomposition. Yong and Matsumura[5,6] affirmed that the nature of the initiating stage depends on the reaction temperature. At low temperatures, the stage is ionic in nature, while at high pressure, it is controlled by radical. During radical initiation, the phenoxy radical formed takes part in two pathways: dimerization via radical coupling, which eventually leads to char formation, and ring opening to produce intermediates, which ultimately leads to the formation of gaseous compounds. These authors rejected the hypothesis that benzene plays a crucial role under these conditions as they detected some signals indicating that benzene is likely formed from phenol via an ionic reaction, not a radical reaction; nevertheless, they also stated that benzene can be formed by the hydrogenation of phenol by the H_2 generated in the own reaction. Goodwin and Rorrer[7] stated that the decomposition of phenol starts via hydrogenation of phenol. Phenol is hydrogenated by the H_2 generated (i) by its own gasification, (ii) in the water–gas shift reaction, and (iii) during the methanation equilibrium, to produce benzene. Later, benzene is gasified to H_2 and CO. Guo et al.[8] reported a similar mechanism in their studies for the gasification of phenol–acetic acid

mixtures. They specified that benzene is also hydrogenated to produce cyclohexane, which acts as the final precursor for gasification. Professor Ning's group has also proposed another mechanism[9], but in their study, the rates of some pathways are affected by the use of ruthenium-based catalysts. Specifically, the use of those catalysts hinders the formation of polycyclic aromatic hydrocarbons, which are precursors to char. Their data suggested two main pathways, (i) the direct gasification of phenol and (ii) its hydrogenation (again with the H_2 generated from its reaction) to cyclohexanol and cyclohexanone, which are also finally converted into gas.

S2) 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 µL sample was extracted with 1 mL of ethyl acetate. Then, 1 µL 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 °C, and the following temperature program was used in the oven: an initial temperature of 50 °C maintained for 5 min, followed by heating at 10 °C/min to 270 °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.

S3) Evolution of the concentrations of CO, CO_2, CH_4, and H_2 for the gasification of a 10^{-1} M phenol solution in a pressure range from 60 to 240 bar
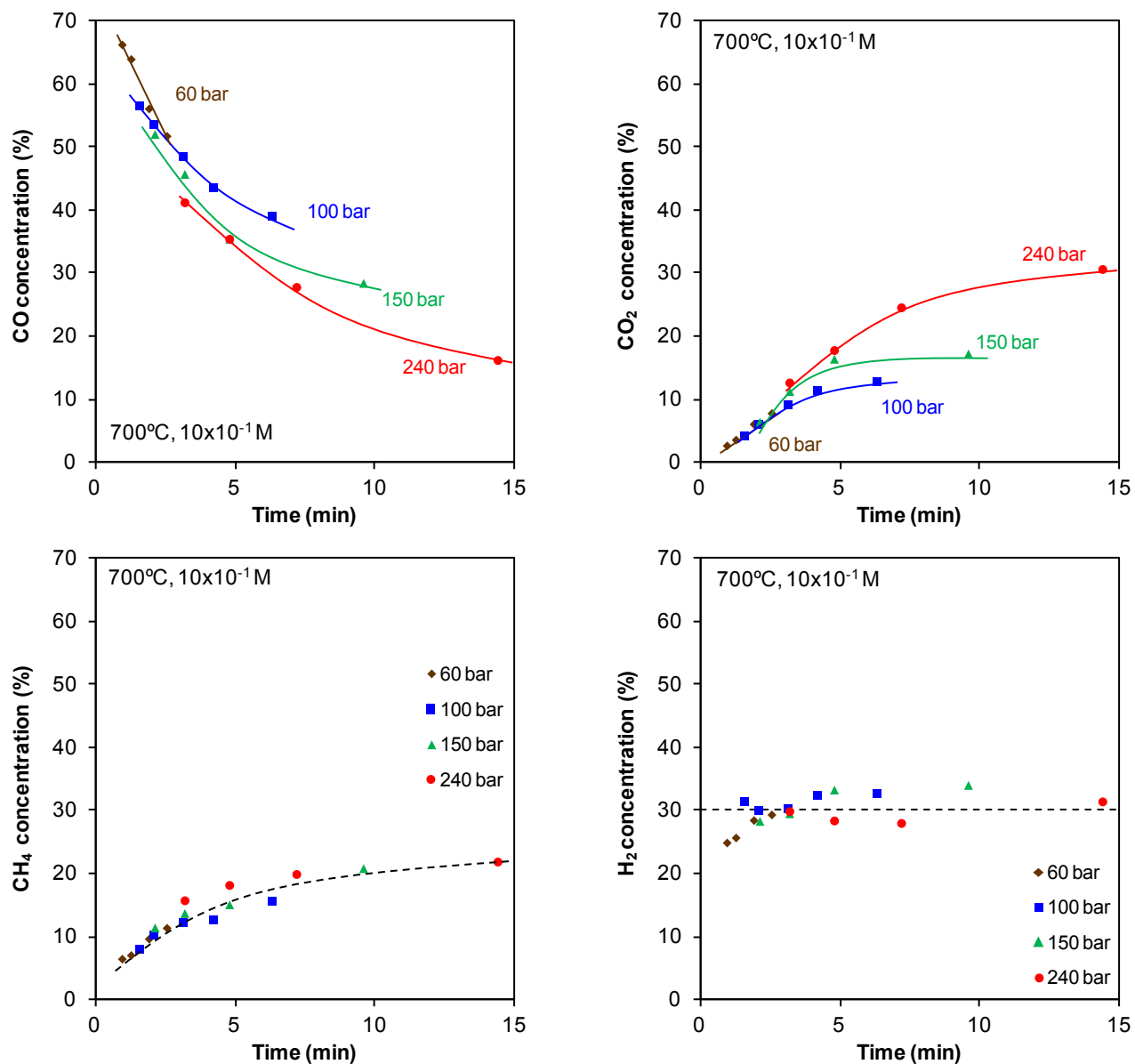

Fig. S1 Evolution of the concentrations of CO, CO_2, CH_4, and H_2 produced during the gasification of a 10^{-1} M phenol solution

S4) Mass balance

The characterization of the gaseous stream produced permits the calculation of the volume of H_2 generated after a concrete reaction time at each of the pressures investigated. The volumes of CO, CO_2, and CH_4 produced can be calculated in a similar manner.

On the other hand, the same volume of H_2 can be theoretically calculated by making a few approximations and considering the different reactions involving H_2. The comparison between the measured and calculated volumes will confirm the accuracy of the approximations.

H_2 can play a role in the following reactions occurring in the phenol–water system:

1. Direct gasification of phenol: H_2 as the product

This is the only pathway generating gases at the start. The number of moles of H_2, CO, CO_2, and CH_4 produced in the gasification of one mole of phenol through this pathway will be always the same at each of the pressures investigated regardless of the reaction time. This relationship can be examined from the data obtained at the start and can be used to calculate the volume of H_2 (and CO, CO_2, and CH4) generated through this pathway with the progress of the reaction.

2. Gasification of polymers naphthalene and phenanthrene: H_2 as the product

The formation and subsequent gasification of polymers to generate H_2 has been confirmed, but scarce information is available about this pathway. However, this reaction does not occur at low pressures and short reaction times as the polymers cannot be gasified by steam. Then, if the calculations are limited to those conditions, the participation of this pathway for the production of H_2 can be omitted.

3. Water–gas shift reaction: H_2 as the product

Considering that the calculations are limited to those conditions under which the formation and gasification of polymers can be ignored, CO_2 is only generated in the direct gasification of phenol and the water–gas shift reaction. Once the total volume of CO_2 produced and the volume of CO_2 produced by the direct gasification of phenol have been calculated, the CO_2 produced by the water–gas shift reaction can be calculated as the difference.

This volume will be the same as that generated by this pathway.

4. Methanation equilibrium: H_2 as the reagent

CH_4 that is produced during the methanation equilibrium (in case it occurs) can be calculated in a manner similar to that calculated in the previous point. The H_2 consumed in this reaction would be three times greater than the CH_4 generated.

In summary, the calculation is expressed as follows:

$$V_{H2,calculated} = V_{H2,gasif\ phenol} + V_{H2,water-gas} - V_{H2,methanation}$$

$$V_{H2,calculated} = V_{H2,gasif\ phenol} + V_{CO2,water-gas} - 3 \cdot V_{CH4,methanation}$$

$$V_{H2,calculated} = V_{H2,gasif\ phenol} + (V_{CO2,total} - V_{CO2,gasif\ phenol}) - 3 \cdot (V_{CH4,total} - V_{CH4,gasif\ phenol})$$

Fig. S2 shows the volumes of H_2 measured and calculated for the gasification of phenol at 60, 100, and 150 bar.
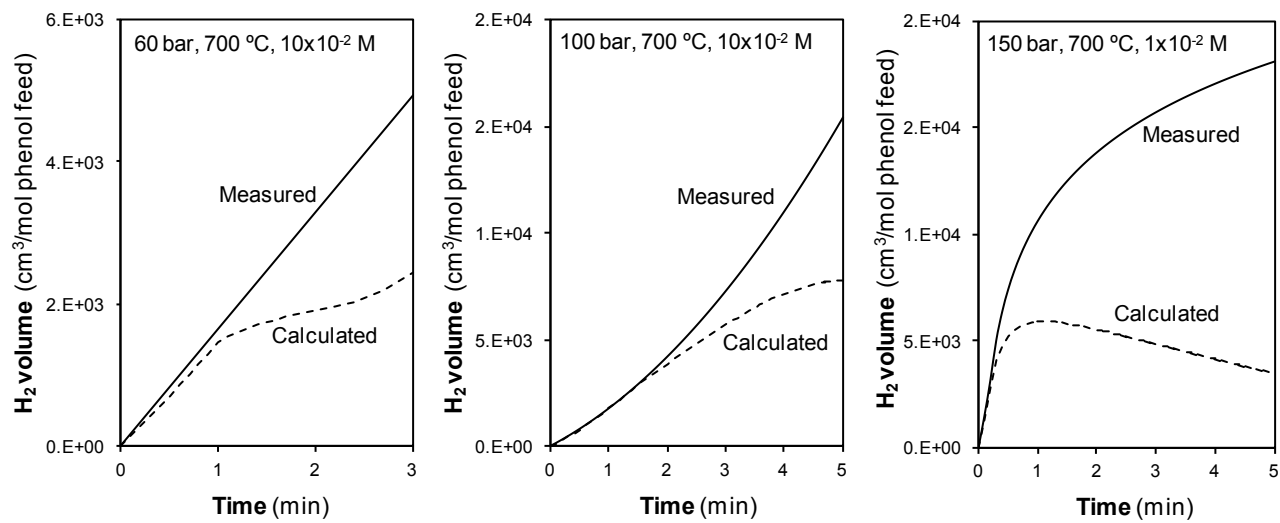
Fig. S2 Volumes of H_2 measured and calculated in case the methanation equilibrium is occurring for gasification carried out at 700 °C and (a) 60, (b) 100, and (c) 150 bar

The volume of H_2 calculated according to the approximations made is less than that experimentally measured. This result is related to the consumption of H_2, which would occur if a part of CH_4 was generated during the methanation equilibrium. Then, the hypothesis that this reaction occurs (or at least that it plays a key role) in the gasification of phenol can be discarded.

References

1 G. J. DiLeo, M. E. Neff and P. E. Savage, *Energy Fuels,* 2007, **21**, 2340-2345.

2 G. J. DiLeo, M. E. Neff, S. Kim and P. E. Savage, *Energy Fuels,* 2008, **22**, 871-877.

3 C. M. Huelsman and P. E. Savage, *Phys. Chem. Chem. Phys.,* 2012, **14**, 2900-2910.

4 C. M. Huelsman and P. E. Savage, *J. Supercrit. Fluid.,* 2013, **81**, 200-209.

5 T. L. K. Yong and Y. Matsumura, *Sekiyu Gakkaishi-Journal of the Japan Petroleum Institute,* 2013, **56**, 331-343.

6 T. L. K. Yong and Y. Matsumura, *J. Supercrit. Fluid.,* 2014, **87**, 73-82.

7 A. K. Goodwin and G. L. Rorrer, *Energy Fuels,* 2009, **23**, 3818-3825.

8 Y. Guo, S. Wang, Y. Wang, J. Zhang, D. Xu and Y. Gong, *Int. J. Hydrogen Energy,* 2012, **37**, 2278-2286.

9 Q. Guan, X. Huang, J. Liu, J. Gu, R. Miao, Q. Chen and P. Ning, *Chem. Eng. J.,* 2016, **283**, 358-365.