

# Biogas valorisation through catalytic decomposition to produce synthesis gas and carbon nanofibres

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## OBJECTIVES AND NOVELTY

Traditionally, biogas has been considered a non-value by-product which was generally burned in flares. Most recently, different alternatives for biogas utilization have been proposed such as heat, electricity or bio-methane production. However, from an economical point of view, the aforementioned applications depend on government feed in tariff and therefore renewable energy producers face an unstable scenario. For that reason, the production of new products from biogas is not only interesting but necessary to diminish the profitability barriers.

In that context, the simultaneous production of syngas and carbon nanofilaments is proposed (Figure 1). On the one hand, syngas constitutes the base of the C1 chemistry and depending on its  $H_2:CO$  ratio it can be used to produce methanol, dimethyl ether, liquid hydrocarbons or  $H_2$ . On the other hand, carbon nanofilaments are high added value material due to their unique properties (thermal and electricity conductivity and textural properties) that make them a promising material as catalyst support, synthetic graphite or graphene precursor or additive in polymer composites. This process, in which syngas and carbon nanofilaments are simultaneously produced from biogas, has been studied for the first time during the course of this thesis and it has been named "Catalytic Decomposition of Biogas (CDB)". Thus, the purpose of the thesis work was to study the technical viability of the biogas valorisation through catalytic decomposition to obtain syngas and high added value carbon nanofilaments.

## RESULTS

First of all, and due to the research group background, the CDB was compared with the catalytic decomposition of  $CH_4$  (CDM). The presence of  $CO_2$  in the biogas changes the balance of carbon on the surface of the catalyst particles as compared to the CDM. Its presence results in a decrease of surface carbon concentration due to the formation of CO (Figure 1) and as a result, catalyst stability is significantly increased.

Regarding the study of the CDB, different massive catalysts, with an active phase/Al molar ratio of 67:33 (X: Ni, Co or Fe), were synthesized using the fusion method and evaluated according to their activity, stability and amount and quality of the carbonaceous material produced.

The effect of the operating conditions (temperature, space velocity and  $CH_4:CO_2$  ratio) was studied using a Ni-based catalyst. Increasing the value of any of the operating variables provokes an increase of the catalytic activity. At the same time, surface carbon concentration raises up and it is transformed into encapsulating carbon that reduces catalyst stability. It was found that there is a compromise between catalytic activity and stability that maximizes the production of carbon which is, indeed, the main objective. However, with increasing reaction time, the catalyst stability turns into the most decisive factor.

In order to avoid or reduce the use of nickel, two different approaches were considered: the use of alternative active phases (Fe and Co) and the synthesis of bimetallic Ni-Co catalysts. The Fe-based catalyst is not a suitable catalyst for the CDB since high temperatures ( $900\text{ }^\circ\text{C}$ ) are required to achieve similar catalytic activities than those obtained with the Ni catalyst. Besides, both quantity and quality of the carbonaceous material produced are low. The performance of the Co catalyst is closer to that of the Ni based catalyst. Nevertheless, at low temperatures ( $600\text{--}700\text{ }^\circ\text{C}$ ), it is considerably deactivated during the first hour of reaction and as a result, the amount of carbon produced is much lower. Therefore, this catalyst is also not a good alternative to the Ni-based catalyst. Finally, results obtained with an equimolar Ni-Co based catalyst improved those obtained with the Ni-based catalyst. By reducing its nickel content a 50%, similar activity and a greater stability were obtained, allowing the production of greater amounts of carbon nanofilaments with similar characteristics.

Carbon type and carbon nanofilaments structure depend on the operating conditions, being the temperature the most determining variable. An increase of its value considerably reduces the proportion of

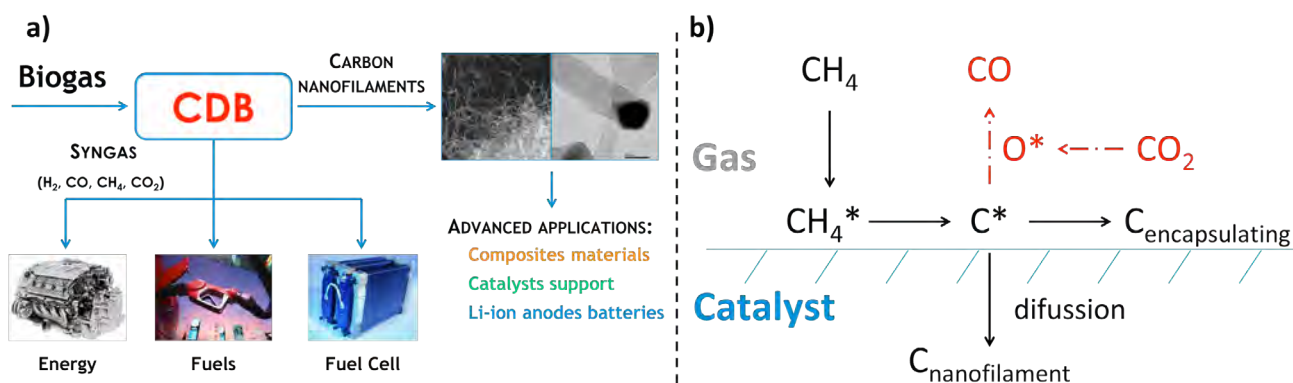
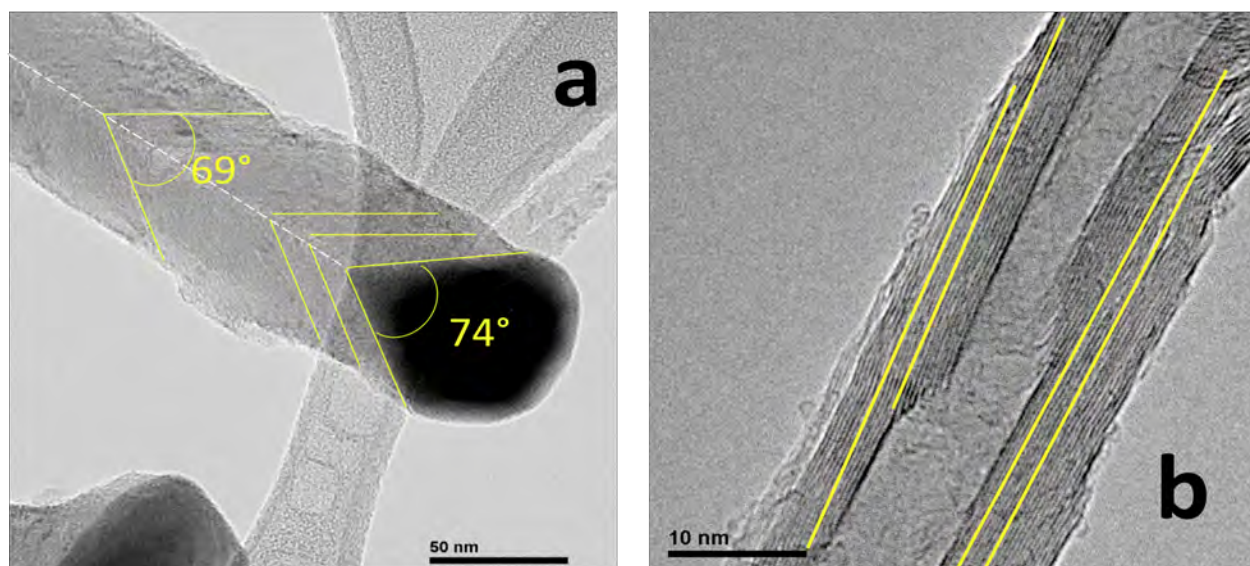


Figure 1. (a) CDB scheme process and (b) simplified mechanism of surface carbon formation/transformation in a Ni catalyst during the CDM and CDB (red steps only take place during the CDB).



**Figure 2.** (a) Fishbone and (b) parallel carbon nanofibres produced in the CDB.

carbon nanofilaments as compared to encapsulating carbon. Therefore, working at 800 and 900 °C is inadvisable. Depending on the operating conditions, the catalyst particles deformation/elongation varies, so that the orientation of the graphene layers. By increasing the value of the operating conditions, carbon nanofilaments evolve from a fishbone type to a parallel type structure (Figure 2).

Since biogas contains minor compounds that can hamper its use, the effect of  $\text{NH}_3$  and siloxanes was studied. Concentrations below 500 ppmv of  $\text{NH}_3$  have no effect on the activity or stability of the catalysts. In contrast, the presence of siloxanes causes progressive deactivation of the catalysts, probably due to the formation of  $\text{SiO}_2$ . Their negative effect could be minimized by reducing temperature and space velocity and the catalytic activity of the catalysts can be maintained for at least 180 minutes even though the concentration used, 50 ppmv ( $287 \text{ mg}_{\text{Si}} \cdot \text{m}^{-3}$ ), is much higher than that of a real biogas ( $10\text{-}20 \text{ mg}_{\text{Si}} \cdot \text{m}^{-3}$ ).

Finally, the scaling-up of the process using a rotary reactor and a fluidized bed reactor was considered. Results show that from the technical point of view the scale-up of the process is feasible. Catalysts activity and stability were similar to those observed in the fixed bed reactor and carbon nanofilaments properties remain invariable. Besides, the preliminary economic study suggested that the use of biogas in the CDB could be a very interesting alternative to energy production through its direct combustion. Incomes from syngas combustion for electricity production are reduced about a 30 % as compared to direct biogas combustion. However, benefits from the simultaneous production of a carbonaceous material with high added value could be two orders of magnitude higher than earnings from energy production.

## CONCLUSIONS

Massive Ni and Ni-Co based catalysts present the best activity and stability and allow to produce great amounts of carbon materials composed principally of carbon nanofibres. Carbon type and carbon nanofilaments structure greatly depend on the active phase and the operating conditions, being the temperature the most determining variable. Thus, the

most suitable range to operate is 600-700 °C. Results related to the effect of minor compounds imply that cleaning stages associated with  $\text{NH}_3$  and siloxanes could be probably eliminated if the CDB is scaled-up, thereby reducing process costs. From research conducted in this thesis work, it can be concluded that the CDB for the simultaneous production of syngas and carbon nanofibres is a feasible alternative, both technically and economically, to the production of energy from biogas combustion.

## RELATED PUBLICATIONS

- [1] Pinilla J.L., de Llobet S., Suelves I., Utrilla R., Lázaro M.J., Moliner R. Catalytic decomposition of methane and methane/ $\text{CO}_2$  mixtures to produce synthesis gas and nanostructured carbonaceous materials. *Fuel* 2011; 90, 2245-2253.
- [2] de Llobet S., Pinilla J.L., Lázaro M.J., Moliner R., Suelves I. Catalytic decomposition of biogas to produce  $\text{H}_2$ -rich fuel gas and carbon nanofibers. Parametric study and characterization. *Int. J. Hydr. Energy* 2012; 37, 7067-7076.
- [3] de Llobet S., Pinilla J.L., Lázaro M.J., Moliner R., Suelves I.  $\text{CH}_4$  and  $\text{CO}_2$  partial pressures influence and deactivation study on the Catalytic Decomposition of Biogas over a Ni catalyst. *Fuel* 2013; 111, 778-783.
- [4] De Llobet S., Purón H., Pinilla J.L., Moliner R., Millán M., Suelves I., Tailored synthesis of organised mesoporous aluminas prepared by non-ionic surfactant templating using a Box-Wilson CCF design. *Micro. Meso. Mat.* 2013; 179, 69-77.
- [5] de Llobet S., Pinilla J.L., Moliner R., Suelves I., Arroyo J., Moreno F., Muñoz M., Monné C., Cameán I., Ramos A., Cuesta N., García A.B. Catalytic decomposition of biogas to produce hydrogen rich fuels for SI engines and valuable nanocarbons. *Int. J. Hydro. Energy* 2013; 38, 15084-15091.
- [6] de Llobet S., Pinilla J.L., Moliner R., Suelves I. Relationship between carbon morphology and catalyst deactivation in the catalytic decomposition of biogas using Ni, Co and Fe based catalysts. *Fuel* 2015; 139, 71-78.
- [7] de Llobet S., Pinilla J.L., Moliner R., Suelves I. Effect of the synthesis conditions of Ni/ $\text{Al}_2\text{O}_3$  catalysts on the biogas decomposition to produce  $\text{H}_2$ -rich gas and carbon nanofibers. *Appl. Catal. B: Environ.* 2015; 165, 457-465.

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