Tailored syngas production from residual biomass gasification for the production of synthetic biofuels

Producción de gas de síntesis a partir de gasificación de biomasa de origen residual adecuado para la producción de biocombustibles sintéticos

I. Martínez*, G. Grasa, M.S. Callén, J.M. López, R. Murillo

Instituto de Carboquímica, CSIC. C/Miguel Luesma Castán, 4, 50018 - Zaragoza (España)
* Corresponding author: imartinez@icb.csic.es

Abstract

Synthetic fuel production from renewable energy sources like biomass is gaining importance driven by the ambitious targets for reducing greenhouse gas emissions worldwide. Sorption enhanced gasification (SEG) proposes carrying out the gasification of biomass in the presence of a CO_2 sorbent, which allows producing a syngas with a suitable composition for a subsequent synthetic fuel production step. The Environmental Research Group of ICB-CSIC is involved in the assessment of this enhanced gasification process focused on residual biomass as a feedstock, analysing the influence of the main operating parameters (i.e. temperature, steam excess, residence time, ..) in the different products obtained (gas, solids and tar). This work has been initiated in the framework of the EU H2020 Programme project FLEDGED [1] and it is going to be continued throughout the recently assigned WASYNG project, funded by the Spanish Ministry of Science, Innovation and Universities. In this work, some of the results obtained for one of the feedstocks studied are presented.

Resumen

La producción de biocombustibles sintéticos a partir de energías renovables como la biomasa constituye una de las principales soluciones para conseguir reducir de forma notable las emisiones de gases de efecto invernadero a nivel mundial. En concreto, la gasificación indirecta de biomasa con vapor en presencia de un sorbente de CO_2 permite producir un gas de síntesis con la composición adecuada para un proceso posterior de síntesis de un biocombustible. El grupo de Investigaciones Medioambientales del ICB-CSIC se encuentra investigando este proceso de gasificación aplicado a biomasas de origen residual, estudiando la influencia de las principales variables de operación (tales como la temperatura, exceso de vapor, tiempo de residencia…) en los principales productos del proceso (gas, sólidos y alquitranes). Esta investigación ha comenzado en el marco del proyecto Europeo FLEDGED del programa H2020 [1] y continuará en el marco del recién asignado proyecto WASYING, financiado por el Ministerio de Ciencia, Innovación y Universidades. En este trabajo se muestran algunos de los resultados obtenidos para una de las biomasas analizadas hasta el momento.

1. Introduction

Production of synthetic fuels from biomass has an important role to play in the decarbonisation of the transport sector [2], as well as in the replacement of fossil fuels in common applications like heat and power production [3]. Steam gasification is one of the thermochemical processes with the greatest potential for obtaining synthetic fuels from a solid fuel [4], especially indirect (or allothermal) gasification in a dual fluidised bed system [5]. In this indirect gasification, the energy needed for the endothermic gasification reactions is provided by the circulating material from a high temperature secondary reactor. Unconverted char leaving the gasifier is burnt in this secondary reactor in order to raise the temperature of the circulating solid that supplies the energy requirement in the gasifier. Typically, two fluidized bed reactors are used in this indirect gasification system, i.e. a bubbling fluidized bed reactor operating as gasifier and a circulating fluidized bed reactor as combustor.

Solid heat material circulating between gasifier and combustor reactors can act exclusively as a heat carrier (i.e. sand) or be a reactive material that takes part in the gasification process. When using a CaO-based CO_2 sorbent as a circulating material, a sorption enhanced gasification (SEG) process results as depicted in Figure 1. In this case, the CaO reacts with the CO_2 produced according to the exothermic carbonation reaction of CaO (i.e., $CaO_{(s)}+CO_{2(g)} \leftrightarrow CaCO_{3(s)}$), shifting in this way gasification and water gas shift reactions towards hydrogen production [6]. In the SEG process, the gasifier is typically operated at 650-750 ºC, which is significantly lower than those used in conventional gasification systems or in indirect gasification with olivine [7]. Despite this fact, CaO has demonstrated proper catalytic properties towards tar cracking and H_2 contents as high as 75 %vol. (dry basis) have been reached with this gasification concept thanks to the favorable effect of the carbonation reaction on the gasification reactions equilibrium.

Depending on the synthetic biofuel to be produced downstream and the catalyst used, the relative amount of H_2, CO and CO_2 in the syngas should be conveniently adjusted. Typically, the module M (defined as the molar ratio $(H_2\text{-}CO_2)/(CO+CO_2)$) or the H_2/CO molar ratio are calculated for a syngas when assessing their suitability for a downstream
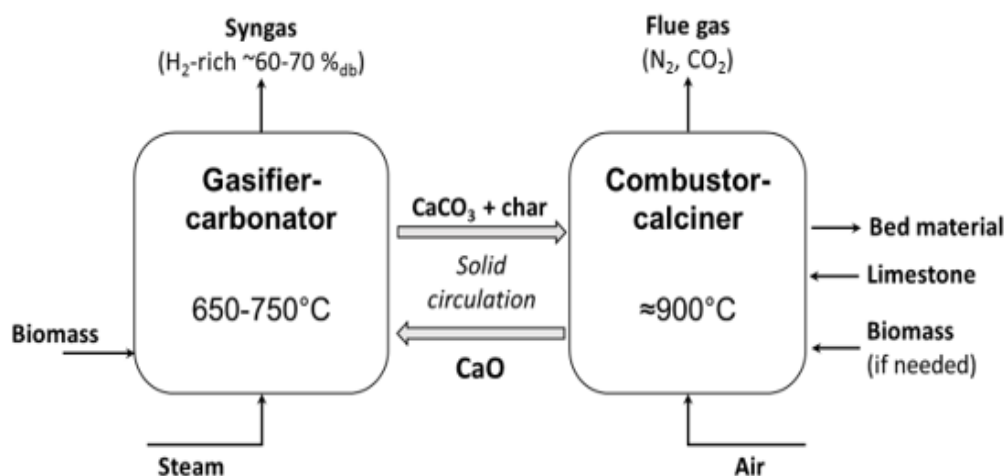
Figure 1. Scheme of the sorption enhanced gasification (SEG) process.

Figura 1. Esquema conceptual del proceso de gasifiación en presencia de un sorbente de CO_2.

synthesis process. For example, in case of biofuels like dimethyl-ether (DME), methanol or Fischer-Tropsch biodiesel, the final H/C ratio is around 2, and therefore such M-module or H_2/CO ratio in the synthesis gas would be needed. However, if focusing on a methanation process, an M-module of 3 will be preferred instead. Adjusting the syngas composition to an adequate M-module or H_2/CO ratio in the syngas produced in the gasifier will be advantageous from an operation and economic points of view, since not only the performance of the catalytic process placed downstream would be optimized but also the conditioning steps before the catalytic synthesis process would be greatly simplified.

One of the inherent advantages of the SEG towards synthetic biofuel production is that it is possible to adjust the composition of the syngas obtained in the gasifier acting in the CO_2 separated in this reactor [10]. In a large scale dual fluidized bed system like that depicted in Figure 1, the amount of CO_2 separated, and ultimately the relative amount of H_2, CO and CO_2 in the syngas, can be regulated by means of the temperature (i.e. solid circulation), the CO_2 carrying capacity of the circulating sorbent and/or the solid inventory in the gasifier. However, it is important to study how the system behaves under such conditions in terms of char conversion, tar yield and composition, syngas quality or the presence of impurities in the syngas. In this sense, the Environmental Research group of ICB-CSIC is actually involved in the H2020 project FLEDGED [1] whose objective is to develop a highly intensive and flexible process for DME production based on the SEG of biomass. In the framework of this project, the role of the Environmental Research group is to assess the SEG process for different biomass based feedstocks in a 25 kWth bubbling fluidized bed (BFB) gasifier for determining the performance of the process in terms of the aforementioned aspects when modifying the operating conditions for DME production. Moreover, thanks to the experience that is being gained in this project, the group will keep on assessing the performance of this SEG process

when focusing on synthetic natural gas (i.e. methane) production in the the recently assigned WASYNG project (funded by the Spanish Ministry of Science, Innovation and Universities). In this work, some of the results obtained at ICB-CSIC for the gasification of a residual biomass in a SEG process are presented and discussed.

2. Study of the sorption enhanced gasification process in a 25 kW$_{th}$ bubbling fluidised bed reactor (BFB)

2.1 Gasifier feedstocks

In the framework of the FLEDGED project up to six different biomass based feedstocks are being tested in a sorption enhanced gasification process at ICB-CSIC. The source of these feedstocks is rather different, e.g. industrial residues, agricultural and forest residues, as well as municipal solid wastes. In this communication the results obtained in the enhanced gasification of a wine making process subproduct are presented, whose ultimate and proximate analyses as well as the calorific value are compiled in Table 1. Particle size of the biomass used ranged between 4.5 mm and 6.8 mm.

Ultimate analysis [%wt., daf basis]		Proximate analysis [%wt.]*	
C	60.3	Moisture	6.30
H	6.6	Volatile matter	65.12
N	2.5	Ash	4.30
S	0.1	Fixed carbon	24.28
O	29.9		
Cl	0.1	LHV [MJ/kg]*	20.51

Table 1. Ultimate and aproximate analyses as well as calorific value of the biomass used.

Tabla 1. Análisis elemental, inmediato y poder calorífico de la biomasa.

CO_2 sorbent used for the experiments was obtained from high-purity limestone calcination (i.e. >98 %wt. of CaO in the calcined residue). The CO_2 carrying capacity of this sorbent along consecutive calcination/carbonation cycles was determined in an atmospheric thermogravimetric analyser (TGA), which has been already described in [11,12] and specifically designed for high temperature multi-cycle testing. It was observed a residual activity of around 0.07 mole of CO_2/mole of CaO after hundreds of cycles for this CO_2 sorbent, while CaO conversion for first carbonation was as high as 0.8 mole of CO_2/mole of CaO.

2.2 BFB plant description

Sorption enhanced gasification (SEG) testing at ICB-CSIC is being undertaken in the 25 kW_{th} bubbling fluidised bed (BFB) gasifier shown in Figure 2. The BFB reactor consists of a 3 m height stainless steel reactor comprising two zones: a bottom dense zone of 1 m height (0.15 m of internal diameter) and a freeboard zone of 2 m height (0.20 m of ID). The reactor is externally heated by means of electrical resistances and insulated with quartz wool. A detailed scheme of the gasification plant is shown in Figure 3. CO_2 sorbent (in calcined form) and biomass are fed separately into the reactor from two independent closed hoppers as shown in the figure. These hoppers are placed over two screw feeders that introduce the solids at the bottom of the reactor (right above

the gas distribution plate). Biomass screw feeder is externally cooled with water in order to prevent its excessive heating due to conduction and so the prompt decomposition of the biomass in the screw. Solids (CaO/$CaCO_3$, unconverted char and ashes) leave the reactor through a lateral overflow (shown schematically in the left-hand side of the reactor in Figure 3), and are collected in a hopper that is periodically discharged during operation, facilitating in this way solid sampling for analysis. This overflow regulates the solid bed inventory in the bottom dense zone of the reactor, which resulted around 5-7 kg depending on the fluidization conditions.

Figure 2. Picture of the BFB gasifier at ICB-CSIC.
Figura 2. Fotografía del gasificador de lecho fluidizado burbujeante en el CIB-CISC.
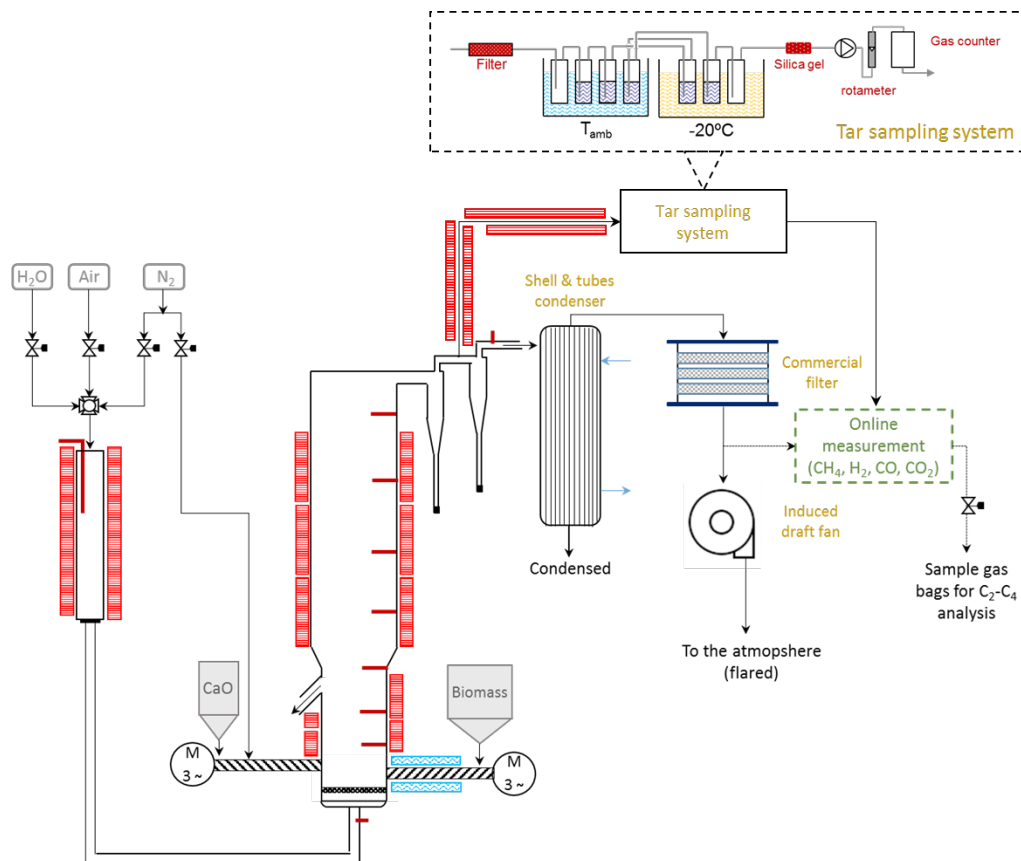

Figure 3. Scheme of the 25 KW_{th} gasification plant at ICB-CSIC (Horizontal red bars indicate the position of thermocouples throughout the main components of the plant).
**Figura 3.** Esquema de la planta de gasificación de 25 KW térmicos situada en el CIB-CSIC (Las barras rojas horizontales indican la posición de los diferentes termopares a lo largo de la planta).

Downstream the gasifier, two high efficiency cyclones are placed in order to separate entrained particles during the operation of the plant. Each cyclone is provided with a hopper where fine particles are accumulated and that can be purged during operation. After passing through the cyclones, syngas is cooled down to around 30 ºC in a shell and tubes condenser, using tap water as coolant. Partially dried cooled syngas is then passed through a commercial dust filter, where fine particles not retained so far are separated. Right after the filter, it is placed a gas sampling line connected to the online gas analyser as indicated in Figure 3. This analyser measures permanent gas concentrations (i.e. CH_4, CO, CO_2, H_2 and O_2) in filtered syngas. Gas sample bags are also taken to quantify higher hydrocarbons (up to C4) by gas chromatography. An off-line method for tar sampling is used based on the specific protocol for biomass gasification units described in [13]. This tar sampling method is based on absorbing tars by flowing the gas through a series of 7 impinger bottles filled with isopropanol, which are placed in two different cooling baths as shown in Figure 1: four impingers (1, 2, 3 and 5) at room temperature and three (4, 6 and 7) at -20 ºC. Gas flow rate sampled through the tar system is regulated by a pump and the total volume passed is measured by a gas-meter before sending the gas to the online analyser. For gravimetric tar determination, an aliquot of 100 ml of the resulting mixture of isopropanol with tars is concentrated in a rotary evaporator until dryness at controlled temperature and vacuum. Chemical composition of the different tar compounds in both the isopropanol with tars mixture as well as the gravimetric tar resulting from evaporation was determined using a Varian CP-3800 gas chromatograph connected to a Saturn 2200 Ion Trap Mass Spectrometer (GS-MS). The identification and quantification of compounds was carried out by external standard calibration for a total of 22 compounds. Finally, the moisture present in the syngas, which is condensed in the mixture of isopropanol with tars obtained in the tar sampling, is determined using the Karl-Fischer titration method.

3. Results and discussion

Figure 4 shows the results obtained about syngas composition and M-module in terms of gasification temperature at constant molar steam-to-carbon ratio. For the experiments performed in the BFB facility, solid residence time was sufficiently high for the CO_2 sorbent to fulfil its maximum CO_2 carrying capacity in every test (it was observed in TGA that the maximum CO_2 carrying capacity was attained in just 2-3 min). Therefore, the amount of CO_2 separated will depend on the sorbent-to-biomass ratio fed to the reactor. Concerning the CO_2 concentration in the gas phase, this will be exclusively affected by the operating temperature of the gasifier through the carbonation reaction equilibrium, i.e. larger CO_2 concentration as temperature increases (see Figure 4 (top)). The same behaviour would be observed in a large-scale dual fluidised bed system (i.e. interconnected gasifier

and combustor reactors) where the temperature of the gasifier is controlled by means of CaO circulation between reactors. In this dual system, increasing the operating temperature in the gasifier is made by increasing the solid circulation from the high temperature combustor/calciner. This means that CaO availability in the gasifier would be so high that the carbonation reaction equilibrium is the limiting factor on the amount of CO_2 captured. Regarding to the CO concentration, its behaviour is correlated to that of the CO_2 through the water gas shift reaction (i.e., $CO+H_2O \leftrightarrow CO_2+H_2$), and it decreases as CO_2 concentration decreases, and vice versa, as appreciated in Figure 4 (left). Because of these trends, the M-module in the syngas reaches their maximum values when going down in the gasification temperature as depicted in Figure 4 (bottom). Looking into the results shown in this figure, the gasification temperature that would allow reaching an M-module of 2 that is suitable for a subsequent DME synthesis process, is close to 730 ºC for the steam-to-carbon ratio of 1.5 working with a thermal input of biomass in the gasifier of 21 kW. However, when looking for CH_4 synthesis in a subsequent methanation process, higher M-modules close to 3 will therefore be required and so gasification temperatures below 700 ºC (out of the range shown in Figure 4 (top)) will be preferred.
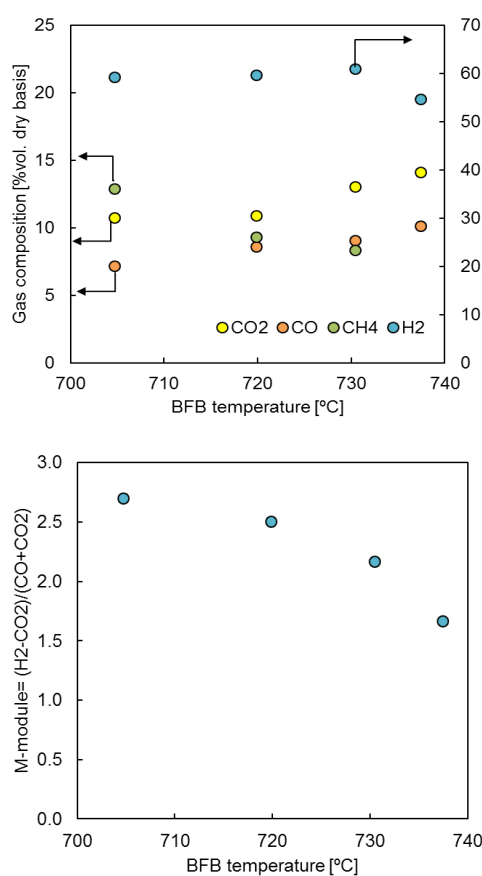

Figure 4. (top) Permanent gas composition (in dry basis) and (bottom) M-module obtained in the syngas for diferent gasification tempertures, keeping constant the molar steam-to-carbon ratio equal to 1.5 for a thermal input of biomass of 21 KW.

Figura 4. (arriba) Concentración de los gases permanentes (en base seca) y (abajo) módulo M en el gas de síntesis al variar la temperatura de operación del gasificador, manteniendo constante la relación molar vapor/carbono igual a 1.5 para un aporte de biomasa de 21 KW.

Figure 5 (left) shows the influence of the gasification temperature on the gas yield and fixed carbon conversion for the steam-to-carbon ratio of 1.5 using 21 kW of biomass thermal input. As noticed, fixed carbon conversion is favoured with the temperature and so contributes to the increase in the gas yield production.

In addition to the effect of the operating temperature of the BFB, solid residence time of the particles in the gasifier can be greatly changed through the solid feeding rates to the reactor. As appreciated in Figure 5 (left), increasing the solid residence time in the reactor by means of reducing proportionally the feeding flows of biomass and CO_2 sorbent into the BFB reactor influences noticeably fixed carbon conversion and, ultimately, the gas yield. An increase of about 60 % in the solid residence time in the gasifier makes the fixed carbon conversion to increment from around 40 % to almost 63 % while the temperature and the steam-to-carbon ratio remained constant and equal to 738ºC and 1.5, respectively. Such increase in the fixed carbon conversion translates into a larger syngas yield of 1.12 Nm^3/kg biomass. In Figure 5 (right) it is shown the gas yield and fixed carbon conversion when modifying the steam-to-carbon ratio at BFB inlet from 1.5 to 1.0, which resulted in slightly different temperatures in the gasifier. As noticed, such reduced increase in temperature of about 20 ºC has a greater impact on the fixed carbon conversion than the excess of steam used for the gasification, which changed from around 55 %vol. of H_2O in the syngas for the test with a steam-to-carbon ratio of 1.5 to around 40 %vol. when working with a steam-to-carbon ratio of 1.
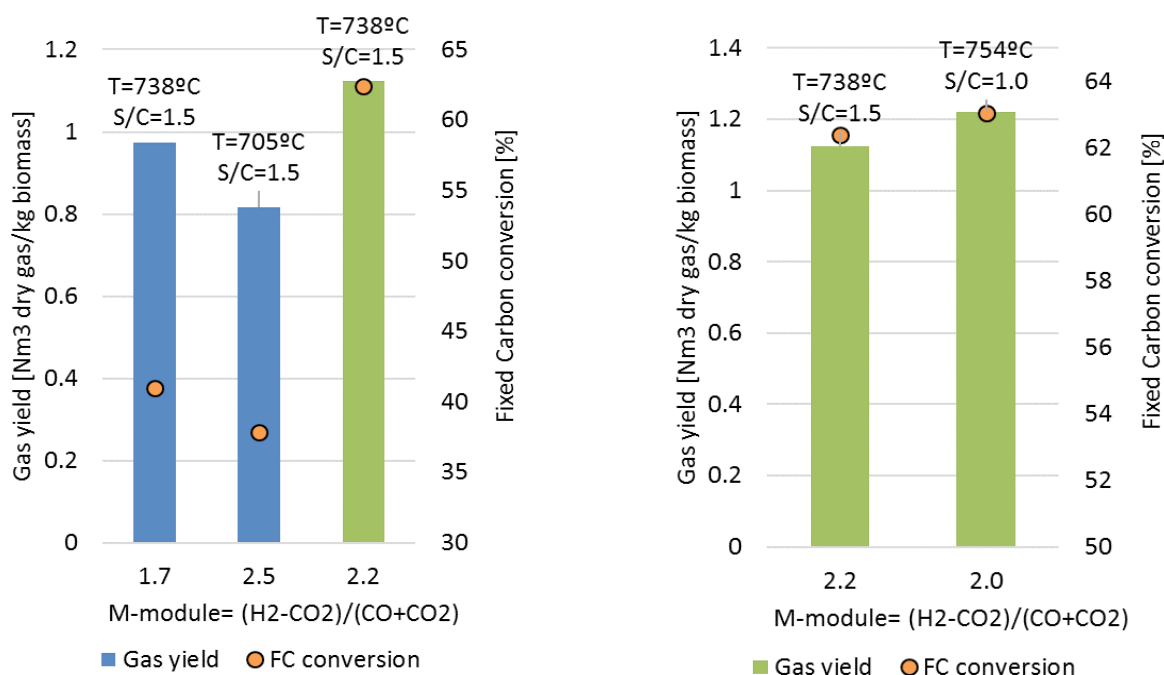

Figure 5. Gas yield, fixed carbon (FC) conversion and M-module obtained for sorption enhanced gasification test under different operating conditions of temperature and steam-to-carbon ratios (blue bars correspond to test with a biomass thermal input of 21 KW, i. e. shorter residence times, and green lines to reduced biomass input of 13 KW).

Figura 5. Producción de gas, conversión de carbón fijo y módulo M obtenidos en los experimentos de gasificación mejorada de biomasa en distintas condiciones de temperatura y relación vapor/carbono (las barras azules se corresponden un aporte térmico de biomasa de 21 KW, lo que equivale a menores tiempos de residencia en el reactor, y las barras verdes con un aporte de biomasa de 13 KW).

In addition to the syngas composition and char conversion, knowledge about tar amount and its composition is important for designing the syngas cleaning system, especially when looking for a downstream catalytic synthesis process for the production of chemicals. Larger tar amounts are expected when operating at low gasification temperatures (i.e. about 650ºC) for this enhanced gasification process due to the increase in the aromatic compounds precursors (e.g. ethylene) concentration detected under such conditions. Gravimetric tar yield of around 21 g/Nm^3 of dry gas was detected at 650 ºC and a molar steam-to-carbon ratio of 1.5. Figure 6 shows the GS-MS chromatograms for the collected tar (i.e. mixture of isopropanol with tars obtained in the tar sampling system in Figure 2) and the gravimetric tar. It is observed in this figure that while in the collected tar the most volatile compounds (benzene, toluene and xylenes) were the predominant compounds, in the gravimetric tar this fraction disappeared, being phenols and substituted phenols the most abundant compounds. Some polycyclic aromatic hydrocarbons (PAH) were also present in the gravimetric tar (GC-MS) with naphthalene and phenanthrene as dominant PAH.
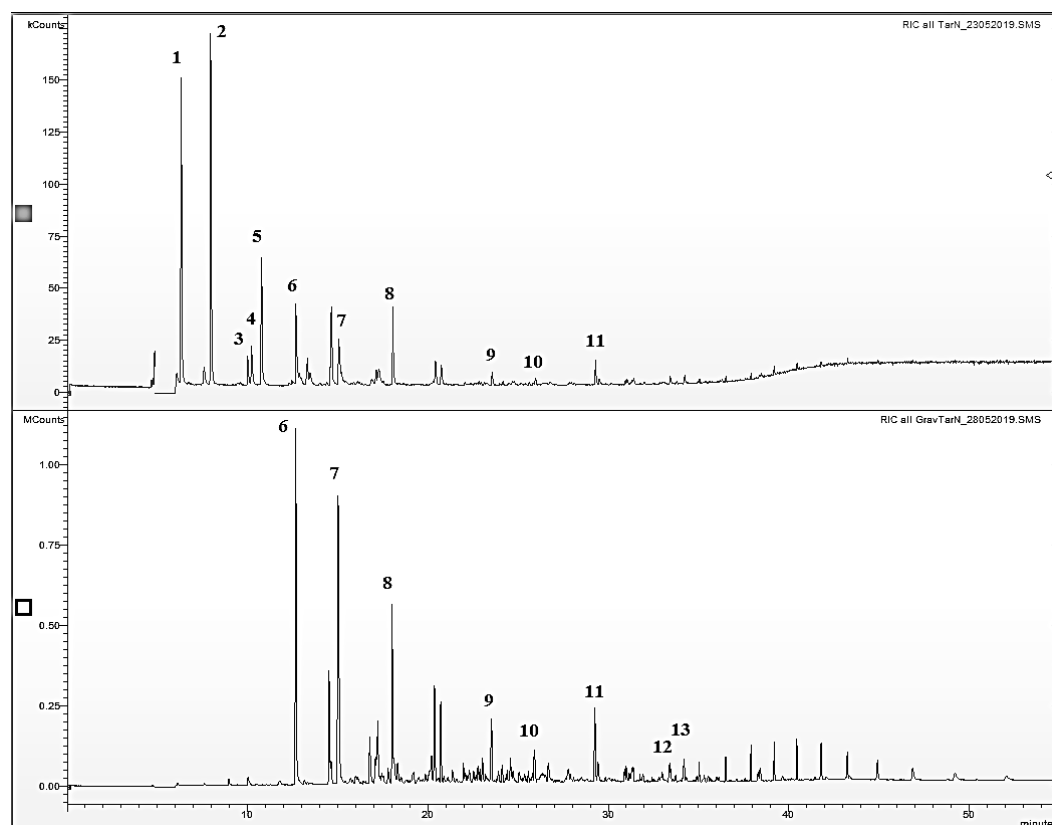
Figure 6. Chromatrogram corresponding to collected (up) and gravimetric tars (down) obtained by GS-MS. Identified compounds: 1=Benzene, 2=Toluene, 3=Ethylbenzene, 4=p+m-Xylene, 5=o-Xylene, 6=Phenol, 7=4-Methylphenol, 8=Napthalene, 9=Acenapthylene, 10=Fluorene, 11=Phenanthrene, 12=Flouranthene and 13=Pyrene.

Figura 6. Cromatograma correspondiente a la disolución de isopopranol + alquitran (superior) y al alquitran gravimétrico (inferior) obtenido mediante GS-MS. Compuestos identificados: 1=Benceno, 2=Tolueno, 3=Etil benceno, 4=p+m-Xileno, 5=o-Xileno, 6=Fenol, 7=4-Metil fenol, 8=Naftaleno, 9=Acenaftileno, 10=Fluoreno, 11=Fenantreno, 12=Flouranteno and 13=Pireno.

Acknowledgements

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