

Assessment of Pilot Scale Pyrolysis Gas Production as Fuel for Cogeneration

Michelle Romero^{a*}, Boris German^a, Daniel Rivadeneira^a, Diego Chulde^a, Andres Chico – Proano^{b,c}, Ricardo A. Narváez C^{e,a}, Javier Martínez – Gómez^d

^aInstituto de Investigación Geológico y Energético, Av. de la República E7-263 y Diego de Almagro, Quito-Ecuador.

^bDepartment of Chemical Engineering, University College London, Torrington Place, London-United Kingdom.

^cDepartamento de Ingeniería Química, Escuela Politécnica Nacional, Ladrón de Guevara E11-253, Quito-Ecuador.

^dUniversidad Internacional SEK Ecuador, Quito-Ecuador.

^eUniversidad Central del Ecuador, UCE-GIIP, EC170521, Quito-Ecuador.

mishuromero@hotmail.com

Amongst the different waste-to-energy technologies that are available, cogeneration presents an opportunity to reduce fossil fuels consumption and the costs associated with electricity use. The addition of a pyrolysis unit to the cogeneration system allows the simultaneous use of pyrolysis gases for electricity generation, and the production of useful byproducts. Since the calorific value of biofuels affects the efficiency of cogeneration systems, it is relevant to determine the pyrolysis conditions that maximize the calorific value of the pyrolysis gas used in cogeneration. In this sense, the present study aims to explore the effect of different processing temperatures over the calorific value of pyrolysis gases in a pilot-scale case with the purpose of adding this component in cogeneration. In such a context, a single screw pyrolyzer was operated at 0.073 MPa using 3.5 kg/min of palm kernel shells as feedstock. Different pyrolysis temperatures were evaluated once the process achieved steady conditions (550, 650, and 750 °C). Since the scope of this work is the gaseous outputs, the resulting pyrolysis gas samples were cooled down and analyzed with gas chromatography. The results show that higher pyrolysis temperatures are associated with higher energy contents. The pyrolysis gas obtained at 750 °C showed a calorific value of 14.01 MJ / Nm³.

1. Introduction

One of the most abundant biomass residues in the world comes from the palm oil industry which produced around 76 million metric tons (Mmt) of palm oil in 2020 (The Statistics Portal, 2021). Every ton of processed palm generates approximately 40% of solid wastes. This is related to a worldwide production of approximately 136 Mmt of palm waste in the last year. The energy use of this waste through cogeneration could cover part of the high electricity demand of this industry (75 - 100 kWh / ton of palm oil). Moreover, this type of waste exploitation could reduce the costs associated with its storage and final disposal (Abdullah and Sulaim, 2013). Cogeneration consists of the combined production of electrical and thermal energy from a single thermochemical process. Amongst the available thermochemical processes for transforming biomass into energy, pyrolysis (decomposition of matter in the absence of oxygen) is the most used. Pyrolysis allows maximizing the yield of the desired product by varying operating conditions such as temperature, residence time and heating rate (Zaman et al., 2017). Conventional cogeneration systems use gases produced by biomass combustion to generate electricity. The addition of a pyrolysis unit to the cogeneration system allows the simultaneous production of pyrolysis gases for the generation of electricity and related byproducts such as biochar and bio-oil. (Fedyukhin et al., 2013).

From the operational point of view, the main parameters that influence the composition and performance of the pyrolysis products are the temperature and the residence time of the biomass in the reactor. Synthesis gas (syngas) produced by biomass pyrolysis is mainly composed of CO, CO₂, CH₄ and H₂. Syngas has a medium-low calorific value that is highly dependent on the operational conditions of the process (Hagos et al., 2016).

However, there is limited research on the composition, calorific value, and energy recovery potential of syngas produced from palm waste pyrolysis. Hence, the objective of this study is to explore the effect of different processing temperatures on the calorific value of pyrolysis gases in a pilot-scale case, with a view to its use in cogeneration.

2. Materials and methods

In this study, samples of palm residues, specifically palm kernel shells (PKS), obtained from the company "Procepalma" (Ecuador) were evaluated. Procepalma is located at km 21 via Quinindé (0°7'5.664 "S 79°15'24.588" W) of the city of Santo Domingo, province of Santo Domingo de los Tsáchilas, Ecuador. The sampling was carried out by using the BS EN 14778 standard that establishes the guidelines for sampling solid fuels from residual biomass. The methodology used for the development of this study is described below.

2.1 Waste characterization

The samples were quartered and subsequently subjected to a size reduction using an Udy Corporation model 3010-014 blade mill, according to the BS EN 14780 standard. The moisture content was determined according to the BS EN 18134-1 standard. A Memmert model SN55 stove was used for such assay. The content of volatile matter and ash were determined according to BS EN 15148 and BS EN 18122, correspondingly. The laboratory equipment for such a task was a Thermo Scientific model F48018 muffle. The elemental analysis was carried out in a Perkin Elmer 2400 automatic elemental analyzer based on the BS EN 16948 standard. The calorific value was measured in an IKA model C2000 calorimeter according to the BS EN 14918 standard.

2.2 Laboratory-scale pyrolysis evaluation

A thermogravimetric analysis of the palm kernel shell was carried out using a Shimadzu model TGA-50 equipment. For the analysis, approximately 13 mg of sample were used. The sample was heated from 20 to 950 °C at a rate of 5 °C/min, under a nitrogen atmosphere with a flow of 50 ml/min.

2.3 Pilot-scale pyrolysis tests

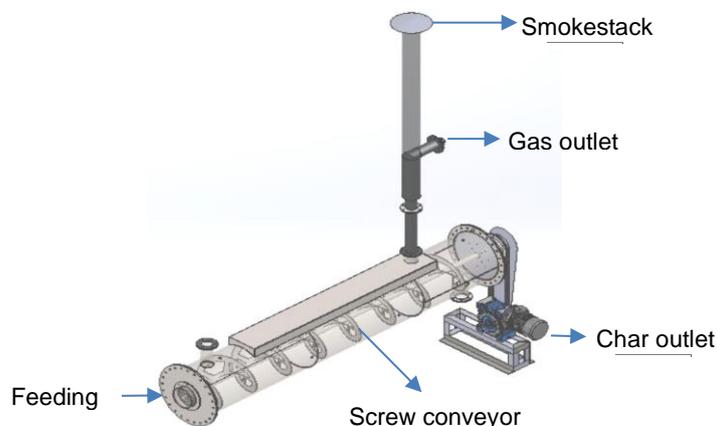


Figure 1: Prototype schematic

For the pilot-scale evaluation, a prototype of a horizontal pyrolyzer with continuous feed was developed and built, with a processing capacity of 4.8 kg/min. The prototype is made of 8 mm thickness AISI 304 stainless steel and is heated by a biomass burner. It is composed by a cylindrical section ($D \times L = 52 \text{ cm} \times 332 \text{ cm}$) that hosts an endless screw for injecting the biomass throughout the core of the reactor. The endless screw is driven by a three-phase motor with an adjustable speed (between 10-30 rpm) for varying the residence time of samples. The main process parameters and peripheral devices are controlled by an open-hardware and software microcontroller board. The temperature profile in the chamber is monitored by four K-type thermocouples located in the pyrolyzer core and at the inlet and outlet of the sample. The horizontal burner prototype design is shown in Figure 1. The pyrolysis tests were carried out at an altitude of 2850 meters above sea level. The feeding rate considered 3.5 kg/min of PKS in each run. The process temperature varied between 550, 650 and 750 °C. The speed of the worm was set at 22.5 rpm. The biomass residence time in the reactor was set to 280 s

by turning the screw on and off during intervals of 20 and 80 s, respectively. Finally, the pyrolysis gases were passed through a condenser and sampled to determine their composition.

2.4 Gas characterization

The outlet gas was analyzed on an Agilent 490 Micro GC micro gas chromatograph, equipped with a TCD detector (Thermal Conductivity Detector). A CP-Molsieve 5A BF 10 m column was used to determine the content of hydrogen, methane, and carbon monoxide in the samples. A PoraPlotU HI UM 10m column was used to determine the content of carbon dioxide, ethane, ethylene, and acetylene. The oven temperature was set at 80 °C. The pressure of the carrier gas, Helium (He) for the 10m PPU column and Argon (Ar) for the 10m MS5Am column was set at 26 psi and 29 psi, correspondingly. The temperature of the injector, detector and sampling line was set at 100 °C. The TCD was calibrated with a standard gas mixture at periodic intervals. Once the chemical composition of the gas was known, the higher calorific value (HCV), both in mass and volume basis, was calculated with the volumetric fractions of each of the component gases and their corresponding calorific value according to the UNE EN ISO 6976 standard.

3. Results and discussion

3.1 Physical-chemical characterization

The physical-chemical characterization of biomass allows defining the conversion process that is most suitable for a proper exploitation. Table 1 shows the results of the physical-chemical characteristics of the palm kernel shell. These results concord with those reported in similar studies (Rugayah et al., 2014; Wang et al., 2018). Regarding moisture content, it is known that moisture contents greater than 30% reduce the temperature reached in the pyrolysis process, producing an incomplete cracking of the hydrocarbons (McKendry, 2002). It is necessary that the raw material has a humidity of around 10 % in order to achieve an adequate ignition of the material (McHenry, 2009). The moisture content found in PKS (10.6 %) could both reduce the energy requirements associated to biomass drying in pre-treatment stages, and increase the calorific value of the produced gas (Demirbaş, 2005).

Table 2: Physical-chemical characteristics of palm kernel shell

Property	Value
Proximal Analysis (dry base)	
Humidity (m/m %)	10.6
Volatile (m/m %)	77.2
Ash (m/m %)	2.3
Fixed carbon ^a (m/m %)	9.9
Calorific value (MJ/kg)	20.8
Elemental Analysis (dry base, m/m %)	
C	54.1
H	6.3
N	0.6
S	0
O	39.0

a: Calculated by difference

The high content of volatile matter (77.18%) shown in the shell confirms its ease for igniting and the significant gas production potential of this type of biomass. In addition, the low ash content (2.31%) implies an advantage for the pyrolysis process, since ash contents higher than 5% cause slag formation problems and blockage of pipes and equipment. It is also important to highlight that the high calorific value, carbon and hydrogen content of the palm kernel shell enable the production of outlet gas with high calorific value and rich in hydrogen. This is because, during the pyrolysis process, the carbon contained within the molecules are released in the form of tars and light gases such as methane. This specific component reacts with water vapor and other gases, generating reforming conditions for the methane and also increasing the hydrogen production yield (Hussain et al., 2019). On the other hand, the low Nitrogen and Sulphur content found in PKS could reduce the emission of SO_x and NO_x pollutants in pyrolysis gaseous streams (Fernandez et al., 2020). Hence, it is possible to affirm that this type of biomass is an environmentally friendly raw material for being used as fuel (Manurung et al., 2009). Considering that the desired characteristics of biomass to be used as feed in the pyrolysis process are a high volatile matter content and a low moisture, ash and sulphur content, palm kernel shell is an appropriate raw material for the pyrolysis process (Noor et al., 2012)

3.2 Laboratory-scale pyrolysis evaluation

The thermal behavior of the PKS, when subjected to the pyrolysis process is presented in Figure 2. Results reported by similar assays (Wang et al., 2018) presented a comparable behaviour.

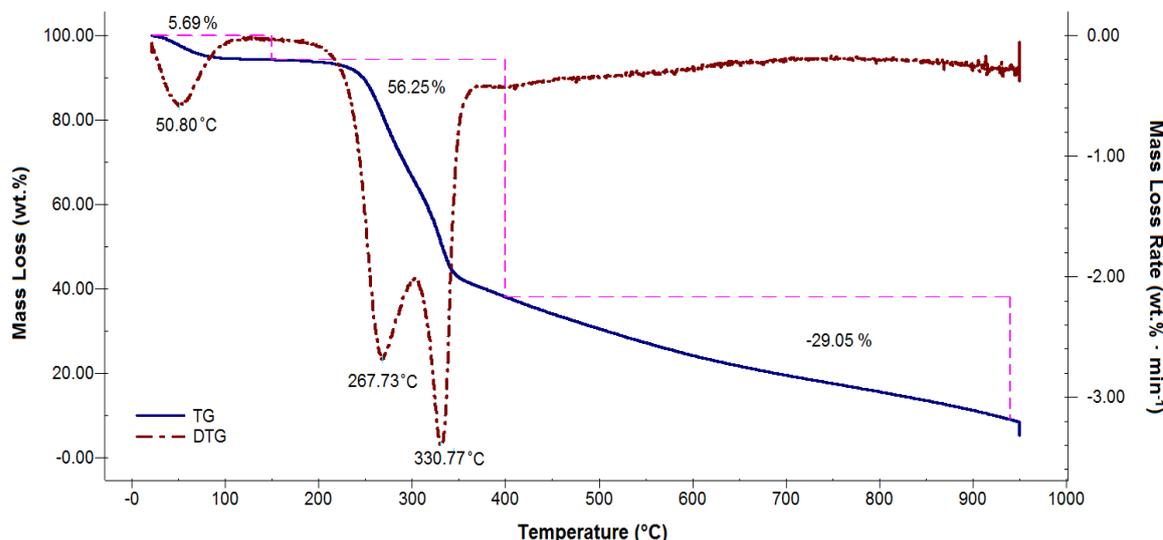


Figure 2. Thermogravimetric analysis of palm kernel shell

Figure 2 shows that weight loss occurred in three main stages. The initial decomposition or first stage was registered between 23 and 150 °C, with a weight loss between 5 and 6%. This fact could be related to the elimination of moisture and part of the light compounds. The second stage took place between 150 and 400 °C; In this stage, approximately 56% of weight was lost and it could be related to the content of volatile matter reported in Table 1. This second stage is recognized as the active zone of pyrolysis and it could be related to the decomposition of hemicellulose, cellulose and lignin. Amongst these three elements, the first to decompose is hemicellulose and it is affirmed it reached the maximum decomposition rate at around 268°C, followed by cellulose at 331°C. The lignin, on the other hand, is believed to decompose slowly throughout the process (González et al., 2009). It is important to emphasize that above 400 °C almost all cellulose decomposes. On the contrary, hemicellulose and lignin do not have the same behavior. During this stage, the structural transformation of biomass delivers a solid product or primary biochar, and also into condensable and non-condensable gases composed by organic compounds (Kim et al., 2010; Sadaka et al., 2014). In the third stage, a slow decomposition was evidenced and it is possible to affirm that it was related to a chemical rearrangement of the primary biochar in order to produce a solid output rich in carbon (Demirbas, 2004).

3.3 Evaluation of pyrolysis on a pilot scale

The experiments carried out in the pyrolysis reactor were the preliminary stage for its potential implementation as a cogeneration facility, which will provide the process with the gas for energy generation. Consequently, the results focused on identifying the operating conditions in the pyrolysis reactor that maximizes the production of gases with a high calorific value. The mass balance of the products delivered a yield of the gaseous products (condensable, and non-condensable compounds) of 83% for the pyrolysis temperature of 550 °C. Moreover, for the conditions of 650 °C and 750 °C, yields of 87 and 90% were obtained, respectively. As the pyrolysis temperature increases from 550 to 750 °C, the mass and energy yields of the gas also increased. This can be related to the secondary cracking of the bio-oils at relatively higher temperatures. In contrast, the mass and energy yields of biochar and bio-oil decreased while increasing the temperature.

3.4 Gas characterization

The results of the compositional analysis of the gas obtained are summarized in Figure 3. The main products obtained being H₂, CH₄, CO, CO₂ and, into a lesser extent, C₂H₆, C₂H₄, C₂H₂, C₃H₈. The results of the latter were synthesized as the C_nH_m product.

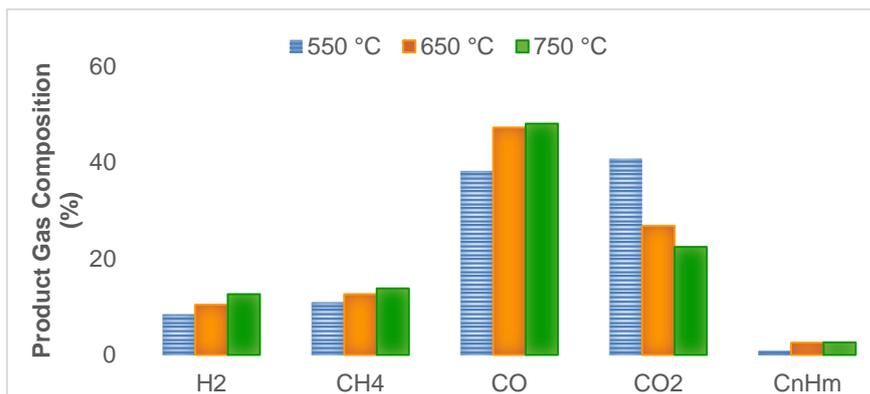


Figure 3. Chemical composition of pyrolysis gas for different reaction temperatures

Figure 3 shows that, when the process was carried out at 750 °C, CO and CO₂ were the dominant species with contents of 48 % and 22 %, correspondingly, followed by CH₄ and H₂ with 14 % and 13 %, respectively. CO₂ is produced because of cracking and reforming reactions of the carboxyl and carbonyl groups during pyrolysis (Zaman et al., 2017). CO₂ content directly affects the potential of the pyrolysis gas as fuel since it not contribute to its calorific value. In this case, the significant content of CO₂ produced can also be directly associated with the large content of lignin found in this biomass type. The presence of lignine hinders the pyrolysis process because of its relatively slow decomposition, which favors the secondary reactions of chemical rearrangement of the solid. This can result in the formation of carbon-rich biochar with high calorific value (Chang et al., 2016). According to this, it is noteworthy the trend of decreasing in CO₂ and the consequent increasing of H₂, CH₄, CO and C_nH_m content as the operating temperature of the pyrolysis process increases, which ultimately increases the calorific value of the gas.

Table 2: Higher calorific value of the pyrolysis gas obtained at different temperatures

Pyrolysis condition temperature	HCV mass basis (MJ/kg)	HCV volume basis (MJ/Nm ³)
550	7.86	10.18
650	11.22	13.15
750	12.58	14.01

The calorific value of the syngas obtained at each temperature is presented in Table 2. These results concord with those reported in similar studies. Velghe et al. (2011a) reported a calorific value between 13-20 MJ/Nm³ for gases produced by pyrolysis of municipal solid waste. Raveendran and Ganesh (1996) reported calorific values, obtained by difference, between 5-16 MJ/kg for gases produced by pyrolysis of different biomass sources. On the other hand, Chen et al. (2003) reported a calorific value between 13-15 MJ/Nm³ for gases produced by pyrolysis of rice straw and sawdust. Larger calorific values in gas outlets can be related to a larger content of C_nH_m compounds, which have larger calorific values than light compounds as methane. However, the presence of high molecular weight hydrocarbons not only delivers higher contents of CO₂ in the gas outlet stream, but also increase the demand of air required for combustion processes, which represents a risk of incomplete combustion. In addition, higher hydrogen contents decrease the amount of required air for complete combustion (Cala et al., 2013). Compared with natural gas, the calorific value of the gas obtained in this work represent already a significant calorific value, equating 40% of it (34.6 MJ/Nm³) (Velghe et al., 2011).

4. Conclusions

On this work, the effect of different processing temperatures on the calorific value of the pyrolysis gases was investigated in a pilot-scale case, with a view to its use in cogeneration. Results show that it is possible to obtain a gaseous product with relevant energy content. Higher operating temperatures led to a higher content of H₂, CH₄, CO and C_nH_m products while CO₂ content was reduced. This increased the calorific value of the output gas. The highest calorific value of the pyrolysis gas was obtained with a composition in volume of 48% CO, 14% CH₄ and 13 % H₂. The largest figure for calorific value was 14.01 MJ/Nm³, obtained at 750 °C. Results showed that the energy potential of the palm kernel shells can be recovered using intermediate-speed pyrolysis technology. A gaseous product is obtained with improved thermal properties for its use as fuel. An energy yield of the gaseous and liquid products of around 80% was obtained for the raw material fed. Turbine operation tests should be carried out in the future, using the obtained gas from this work to determine the efficiency of a

cogeneration unit coupled with a pyrolysis system. Moreover, the development of models that can predict the yield of hydrocarbons from biomass pyrolysis and its energy content are required to evaluate pyrolysis/turbine combined systems efficiency and to determine the optimal conditions of the process (temperature and residence time) that allow producing fuels with ideal properties for cogeneration application.

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