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# Optimal slow pyrolysis of apple pomace reaction conditions for the generation of a feedstock gas for hydrogen production

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## ABSTRACT

This research explores optimal reaction conditions for the generation of gas products, through the slow pyrolysis of apple pomace, to be used as a feedstock for the production of H<sub>2</sub> by the absorption enhanced reforming of methane (AER). Pyrolysis was performed at 300–450 °C and heating rates 5–20 °C/min. Gases, tars and chars were quantified at different heating rates and isothermal conditions. Results indicate that at 400 °C a maximum of 71.5% W of non-condensable volatile matter (NCVM) can be obtained along with 25.4% W of condensable volatile matter (CVM), while only 3% W of residual matter (RM). At these conditions (NCVM) a gas composition of 49.8% CO, 26.8% CO<sub>2</sub> and 23.4% CH<sub>4</sub> (Vol) was generated. A thermodynamic analysis of this product gas was performed under AER through CO<sub>2</sub> absorption by CaO. Calculations using a steam to methane ratio of 3.5 and 3.5 mol of CaO/mol of CH<sub>4</sub> indicate that a maximum H<sub>2</sub> production is achieved at 715 °C containing 73.0% H<sub>2</sub>, 19.1% CO, 5.3% CO<sub>2</sub> and 2.5% CH<sub>4</sub> with no carbon formation.

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## Introduction

The use of biomass for the production of energy has become an important strategy aimed to reduce the harmful environmental impact of today's use of fossil fuels. Energy derived from biomass and solid wastes, has been the heart of many thermochemical and biochemical processes [1]. In thermochemical processes, gasification and pyrolysis has reached greater energy conversions than direct combustion [2]. Furthermore, biofuels produced from various lignocellulosic materials such as wood, agricultural or forest residues, have the potential to be a valuable substitute (or supplement to

gasoline biofuels) to liquid or gaseous fuels for the transport sector [3]. One specific example of a biomass waste is the apple pomace, which is the residue generated in the process of extraction of apple juice. A complex mixture of shell, seed kernel, calyx, stem and soft tissue compose this waste, which is representative of the pomace, and their composition is mainly cellulose, hemicellulose, lignin and some pectin.

Moreover, a great deal of research has been made focused on flash and vacuum pyrolysis, process conditions and its yield. However, slow pyrolysis has been overlooked, probably because in this kind of processes solid residues are the interested product and condensable and non-condensable products are burned or directly emitted to the atmosphere

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[4] and as a consequence, up to date there are no studies involving the pyrolysis of Mexico's apple pomace. This condensable and non-condensable matter that usually is called bio-oil and bio-gas, respectively; is suitable to be employed as feedstock for hydrogen production [5].

Two main technologies for hydrogen production that have been explored in recent years are biomass steam gasification and biomass slow pyrolysis [6]. It has been reported that fast pyrolysis followed by steam methane reforming of oil delivers less  $H_2$  yield. The  $H_2$  production cost from supercritical water gasification is too high. Compared with fast pyrolysis and supercritical water gasification, steam gasification performs better. While, the efficiency of the steam methane reforming can be enhanced towards the production of hydrogen using the products from the slow pyrolysis of biomass (apple pomace) [7].

Furthermore, in steam reforming reactions of biomass-derived carbohydrates, if  $CO_2$  is removed immediately, according to Le Chatelier principle, its partial pressure decreases and the equilibrium shifts to the direction that favors hydrogen production [8–11]. This makes possible high fuel (i.e.  $CH_4$ ) conversion at relatively low temperatures and production of high quality hydrogen (95%) with only traces of carbon oxides (in the order of 1% vol.). This concept has been called absorption enhanced steam reforming (AESR) [12]. Recent experiments by Yi and Harrison [13] demonstrated that in the presence of an absorbent good conversion and very low concentrations of CO can be achieved even at very low pressures (1 bar) and temperatures (460 °C). A potential absorbent material should have good  $CO_2$  capacity at high temperatures, be easily regenerable and thermally stable to allow a cyclic absorption-desorption process. Experimental studies have demonstrated that in situ carbonation of CaO within the steam reformer is able to generate high  $H_2$  concentrations [9,10]. Thus, this absorbent (CaO) has become a reference absorbent in many of these studies and thermodynamic analyses reported for the AESR process. Therefore, a thermodynamic analysis can be of paramount importance to investigate fundamental reaction parameters influencing the output of  $H_2$ -rich gas from the AERS of non-condensable volatile matter (NCVM) produced from the slow pyrolysis of apple pomace. However, NCVM composition is of great importance, since from this depends the final hydrogen production purity and quantity.

Hence, the present research is aimed to explore optimal reaction conditions for the generation of a gas product (NCVM), through the slow pyrolysis of pomace, to be used as a feedstock for the production of  $H_2$  by the absorption enhanced reforming of methane (AER) process scheme. Furthermore, a thermodynamic analysis will be performed to explore the hydrogen production by the AER of the NCVM.

## Materials and methods

### Sample characterization

Apple pomace samples were collected from the northern state of Chihuahua (Cuauhtémoc, Chihuahua). These were subjected to a drying process, crushed, grounded and sieved to achieve a particle size of 150  $\mu m$ . The elemental and proximal analyzes for the apple pomace sample were performed using a

Carlo Erba EA-1110 elemental analyzer and an atomic emission spectrometer coupled with ICP (ICP Thermo Jarrell Ash IRIS/AP DUO). Lignin, cellulose, and hemicellulose content from the pomace were determined using gravimetric techniques, described in ASTM (E 1756-95, D1106-95) and ASTM (D1103-60). Moisture, volatiles and ash content was determined according to the procedure described in ASTM E (871-82), ASTM (872-82) and ASTM (1755-1795), respectively. In order to obtain homogenous samples at certain particle size (dp), samples were sorted to dimensions:  $dp < 150 \mu m$  (150  $\mu m$ ),  $150 < dp < 180 \mu m$  (180  $\mu m$ ),  $180 < dp < 250 \mu m$  (250  $\mu m$ ), and  $250 < dp < 450 \mu m$  (450  $\mu m$ ).

### Determination of apple pomace pyrolysis parameters

Operating parameters that directly influence biomass pyrolysis are; temperature, particle size (dp), heating rate and residence time [14]. The production of a greater amount of volatile matter was the criterion applied for determining the value of the operating parameters. For this purpose, Thermogravimetric Analysis (TGA) tests were performed in a TA Instruments Q500. TGA conditions employed to find optimal values for temperature and particle size were; a  $N_2$  flowrate of 100  $cm^3/min$  and a heating rate of 10 °C/min. Apple pomace with the same particle size were exposed at different heating rates; 5, 10, 15 and 20 °C/min, in order to verify the effect of the heating rate over the production of volatile matter. Residence time, which was defined as the time required for a 90% volatilization of the sample, was determined by varying isothermal time at different temperatures (pyrolysis in stages) [15]. This was achieved by the combination of the dynamic and isothermal TGA operating modes under the following conditions: particle size of  $420 < dp < 840 \mu m$ , heating rate of 10 °C/min,  $N_2$  flowrate of 100  $cm^3/min$ , isotherms of 150, 200, 250, 300, 350, 400, 450, 500 and 550 °C and residence time of 60 min.

### Quantification of the pyrolysis products

The carbon residue percentage (CR) was obtained from the fractionated pyrolysis performed in the TGA using a residence time of 60 min. The condensable matter was gravimetrically quantified during the pyrolysis and this was performed in a fixed-bed tubular reactor coupled to a condensing system as described in Fig. 1.

The pyrolysis set up was composed of a stainless steel tubular reactor, heated by an electrical furnace under temperatures up to 600 °C and an inert  $N_2$  atmosphere (see Fig. 1). The stainless steel tubular reactor had an internal diameter of 2 cm and a heated length of 27 cm. Apple pomace samples were held with a porous stainless steel frit and quartz wool. Nitrogen was also used as carrier and inert gas. A mass flow controller was used to supply 100  $cm^3/min$  of  $N_2$ . Condensable volatiles are trapped in a copper coil condenser cooled to 2 °C. In order to determine the amount of mass of total condensable volatiles, the weight change of the sample before and after each cycle of the pyrolysis was measured, and this represents the carbon residue (CR). The non-condensable volatile compounds were identified by gas chromatography using a Perkin Elmer Clarus 500. Detection of non-condensable gases (CO,

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