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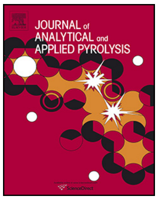

Solar biomass pyrolysis for the production of bio-fuels and chemical commodities

Sergio Morales[a], Rosa Miranda[a,b,*], Diana Bustos[a], Thania Cazares[a], Honghi Tran[b]

[a] Universidad Autónoma de Nuevo León, Facultad de Ciencias Químicas, Chemical Engineering Department, Universidad Ave. S/N, Ciudad Universitaria, San Nicolás de los Garza, 66450 Nuevo León, Mexico
[b] Pulp & Paper Centre, Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, M5S 3E5 Toronto, Ontario, Canada

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ABSTRACT

This study investigated orange-peel pyrolysis due to solar radiation that was applied as a unique source of energy using a parabolic-trough solar concentrator. An optical analysis was conducted using a Monte Carlo ray-tracing method to provide a detailed tridimensional description of the optical performance of the thermo-solar system. The average irradiance of the pyrolytic reactor surface was 15.65 suns. The peak irradiance was very similar to that calculated using the ray-tracing method, confirming that the operational conditions were optimal. The heat balance was analyzed by applying optical and thermodynamic principles. The main heat losses were caused by the reflectivity of the biomass (37.85%) and the difference between the temperatures of the environment and the reactor (36.23%). The solar pyrolytic reactor reached a peak temperature of 465 °C at the middle of the focal line. The total weight loss of the orange peels was 79 wt.% at an average irradiance of 12.55 kW/m^2. Furthermore, substances valuable to the energy, chemical and pharmaceutical industries were identified in the bio-oil that was produced during solar pyrolysis, such as (Z)-9-octadecenamide, diisooctyl phthalate, squalene, D-limonene, and phenol.

1. Introduction

One of the most complex challenges that humanity must face today is managing and halting the climate change produced by the over-exploitation of natural resources. On October 31st, 2011, the global human population included 7 billion inhabitants and it is forecasted to reach 9.3 billion by 2050 [1]. This forewarned large population will surely increase the demand for energetic resources. The use of thermo-solar energy and the production of bio-fuels using biomasses are options that may offer a sustainable solution to the energy needs of the modern human being without compromising the environment.

The two main types of processes that can convert biomasses into useful bio-fuels are thermochemical and biochemical processes. The thermochemical processes include gasification, pyrolysis, liquefaction and combustion [2]. The biochemical processes have conversion efficiencies of between 35 and 50 wt.%, whereas the thermochemical processes have conversion efficiencies of 41–77 wt.% [3]. In addition to transforming the biomass into bioenergetics, these processes can be used to produce almost any product of the petrochemical industry [2]. One of the thermochemical processes with the highest flexibility in terms of the yield and composition of the products that can be obtained is pyrolysis. Pyrolysis of a biomass is defined as the thermal degradation of the biopolymers present in the organic material under an inert oxygen-free atmosphere [4]. This process can be used to produce bio-fuels, bio-oils, biogas and chars in various proportions depending on the type of pyrolysis, the selected reactor and the operational conditions. An advantage of pyrolysis is that it can convert over 60 wt.% of the biomass into a liquid bio-oil [4,5]. However, pyrolysis has the disadvantage of requiring an external energy input to reach the operating temperature, which may range from 300 °C to 650 °C, to promote the formation of liquid products [2]. This external energy input is generally derived from a non-renewable source that has a negative impact on the environment. A possible solution to this problem is to use thermo-solar energy to heat the reactor to obtain solar pyrolysis.

Solar biomass pyrolysis is an endothermic process of converting a biomass in an inert atmosphere in which the required heat

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[*] Corresponding author at: Pulp and Paper Centre, Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, M5S 3E5, Toronto, Ontario, Canada. Tel.: +1 4 1694 67556.
E-mail addresses: rosymirandag@yahoo.com.mx, rosa.miranda@utoronto.ca, rosymirandag@hotmail.com (R. Miranda).

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Nomenclature

I	insolation, W/m^2. Eq. (5)
q_0	concentrated radiation, W/m^2. Eqs. (3) and (4)
c	circumference, m. Eq. (5)
$Q_{absorbed}^{solar}$	absorbed solar energy by the thermo-solar system, J. Eqs. (2) and (3).
$Q_{reactor}$	heat in the reactor, J. Eqs. (2) and (6)
$Q_{biomass}$	heat in the biomass, J. Eqs. (2) and (7)
$Q_{loss\ to\ the\ environment}$	environmental heat loss, J. Eqs. (2) and (8)
Q_{rxn}	reaction heat of the pyrolysis, J. Eqs. (2) and (10)
$\alpha_{reactor}$	absorbance of the reactor, fraction. Eq. (3)
$\alpha_{biomass}$	absorbance of the biomass, fraction. Eq. (3)
$\tau_{reactor}$	transmittance of the reactor, fraction. Eq. (3)
η_{optic}	optic efficiency, %. Eq. (4)
η_{focus}	focusing efficiency, %. Eq. (4)
A	surface area of the reactor, m^2. Eqs. (4) and (8)
t	residence time of the biomass, s. Eqs. (4) and (8)
φ	irradiance across the circumference of the reactor, W/m^2, Eqs. (4) and (5)
T_∞	environmental temperature, °C. Eqs. (6)–(8)
T_f	operational temperature, °C. Eqs. (6)–(9)
$M_{reactor}$	mass of the reactor, kg. Eq. (6).
$M_{biomass}$	mass of the biomass, kg. Eqs. (7) and (10)
$C_{p\ reactor}$	heat capacity of reactor, J/kg °C. Eq. (6)
$C_{p\ biomass}$	dried orange peel heat capacity, J/kg °C. Eq. (7)
h	heat loss coefficient (convection and radiation to the environment), W/m^2 °C. Eqs. (8) and (9)
H_{rxn}	enthalpy of the orange peel pyrolysis per mass unit, J/kg. Eq. (10)
L	Length of the reactor, m
Φ	Diameter of the reactor, in.
FC	Fixed carbon, wt.%

is provided by concentrated solar energy. The direct solar insolation is concentrated and redirected to the pyrolytic reactor by an optical system. This concentrated energy allows the reactor and the biomass to reach pyrolytic temperatures. There are three possible ways to transfer the solar heat to the biomass, as follows: through the walls of the reactor, by applying direct irradiation of the carbonaceous material or by employing an intermediate heat-carrying fluid [6]. When the biomass is directly irradiated, the biomass will become the hottest portion of the system and the reactor will remain at a lower temperature, reducing the rate of secondary decomposition reactions in the gas phase.

Solar biomass pyrolysis may be performed using a thermo-solar system. A thermo-solar system concentrates and redirects the solar radiation from a large area into a smaller one to use this energy as a heating source. Thermo-solar systems consist of 3 main parts, which are the solar concentrator, the solar collector, and a supporting structure. The solar concentrator focalized the solar radiation on the surface of the solar collector, which in this study was a tubular pyrolytic reactor. Both components were mounted on the supporting structure. A summary of the different types of solar concentrators is shown in Table 1. Because a parabolic-trough concentrator produces a focal line of radiation, this apparatus is the ideal option for heating tubular reactors to the temperatures needed for biomass pyrolysis.

The pyrolysis of carbonaceous materials using concentrated radiation has been studied by a few authors (Table 2). The mass loss reported by the authors ranged from 20 to 92 wt.% upon concentrated irradiation. However, most of the studies used coal or cellulose as the raw material and the yields of pyrolytic liquids or main compounds were not reported. Tabatabaie-raissi et al. [16] and Boutin et al. [17,18], who performed cellulose pyrolysis using concentrated radiation emitted by a xenon lamp, obtained a mass loss of 92.1 wt.% and 20.0 wt.%, respectively. Boutin et al. [18] concluded that the relatively low mass loss observed was due the shrinkage of the cellulose that occurred during thermal degradation moving the sample out of the focal point. Beattie et al. [19] pyrolyzed a coal sample using concentrated solar energy. The authors found that pyrolysis of the coal occurred when the irradiation level was greater than 200 W/cm^2, which resulted in 51 wt.% of volatiles and no tar formation. To date, there is scarce information in the literature regarding solar pyrolysis and even less information involving solar pyrolysis of agro industrial waste.

To date, a small number of patents related to solar thermal conversion of biomasses into a bio-fuel have been filed. Most of the related research has focused on the production of hydrogen and carbon monoxide using natural solar radiation. The types of furnaces used include a solar-pump laser, a hybrid solar–syngas system and a solar/microwave system [20–22]. The solar radiation used for these processes has been augmented by conventional heating sources, such as microwaves and plasma; only McAllister [25] and Storey et al. [23] used solar thermal energy as the only heating source for a solar concentrator equipped with actuators [25] or with parabolic mirrors controlled via electric motors [23]. The raw materials generally used range from sisal residues [23], oil shale [24], biomasses, domestic waste, sludge from waste water, fossil coal [24,25] to pure cellulose [20]. The products of the solar processes included fuels [22], olefins and carbon, oil fines [21], H_2 [20,21,25,26], CO_2 [20,21] and vapor, the latter of which was used as a power source [21]. Further analysis of the optics, yields and description of the products of the solar systems has yet to be reported.

The solar production of bio-fuels offers a possible solution for storing solar energy in a chemical compound. Considering that a high-temperature process is used to induce an endothermic reaction in a solar chemical reactor, when energetic products are needed, an exothermic reaction would expel heat in an amount equal to the sum of the energy stored during solar thermal decomposition and photosynthesis [27,28]. This phenomenon allows exploitation of the energy stored in the compound at any place and at any time, even when the solar resource is not available (for instance, during the night or on cloudy days).

The direct use of solar radiation to induce pyrolysis has an advantage over traditional methods in that the process does not require the consumption of fossil fuels or electricity to bring the system to a pyrolytic temperature. Solar pyrolysis is a sustainable solution for the production of biofuels from agro-industrial wastes in cities with a high degree of insolation, such as Monterrey Mexico, which receives approximately 2245 kWh/m^{2}a of sunlight [29].

Citrus fruits are the most abundant crops in the world, with more than 120 million tons/year of oranges, lemons, grapefruits and mandarins produced [30]. In 2010, Mexico produced 4 million tons of orange, of which 40 wt.% (approximately 1.6 million tons) became wet-solid residues of the orange industry [31].

The aim of the present study was to perform optical and thermal analyses of the process of producing a bio-fuel using solar pyrolysis of orange peels. In addition, the bio-oil was characterized. Because orange peels are an agro-industrial waste with a negative impact on the environment, the present project addressed to the need to identify new renewable energy sources and demonstrated a possible approach to solid agro-industrial waste management.

2. Methodology

The methodology of this study involved the eight following steps: sample preparation, sample characterization, solar

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