

HYDROGEN PRODUCTION BY NON-CONVENTIONAL BIOMASS PYROLYSIS PROCESS AND ENVIRONMENTAL IMPACT

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ABSTRACT: The key factor to reducing and controlling of CO₂ from environment, which is the major contributor to global warming, is the use of alternative energy systems that can be used today and may be used in the future as green energy sources. Renewable resources currently account for about 9%-10% of energy consumed in the world and most of this is from hydropower and traditional biomass sources. Each of renewable energy technologies is in a different stage of development and commercialization and all have differences in current and future expected costs, resource availability and potential impact on energy supply. This paper discusses the potential for such integrated systems in response to the critical need for a cleaner energy technology. Several issues relating to renewable energies, environment and sustainable development are examined from both current and future perspectives. On the other hand, biomass is a potential energy resource that can be converted into different forms of energy or energy carrier, such as hydrogen. In this study, also non-conventional biomass sources such as rapeseed, rapeseed cake, and rapeseed meal, had been tested for hydrogen production from biomass pyrolysis process. The influence of biomass microstructure and reducing sugar content on the hydrogen production was studied through a high-energy ball-milling pre-process of the biomass source. The results indicate that the maximum production of hydrogen was obtained at 450°C independently of the biomass source. The biomass microstructure and reducing sugar content does not seem to have an effect on hydrogen production from biomass pyrolysis.

KEY WORDS: Renewable energy technologies, Energy efficiency, Environmental impact, Biomass pyrolysis, Hydrogen production

1. INTRODUCTION

Energy has been a vital input into the economic and social development. In practice, low energy environments are achieved through a combination of measures that include the application of environmental regulations and policy based on the application of environmental science and best practice. The increased availability of reliable and efficient energy systems encourages and stimulates new development alternatives. The energy need is certain to increase with growth in population. Energy sources take many forms, including fossil fuels (petroleum, coal, natural gas), nuclear energy or renewable sources (wind, solar, hydropower, geothermal, biomass, hydrogen, etc). From those, fossil fuels sources are being consumed at a higher rate [1] and the continued use of fossil fuels leads to the increasing concentrations of carbon dioxide (CO₂) in the atmosphere, air pollution and global warming [2]. At present, alternative renewable energy sources are not competitive in terms of cost and production capacity with fossil fuels [3]. The finding of the viable alternative sources of clean energy that to satisfy the demand is and will be one of the biggest challenges. One of the most promising alternative energy technologies is hydrogen production because it is a

renewable, clean and environmentally non-polluting fuel [3]. Hydrogen is a secondary form of energy, it is not free in nature, it is an energy carrier [4] because it can be manufactured like electricity. Hydrogen gas can be use in combustion engines and fuel for electric vehicles due to hydrogen has a higher energy yield of 122 kJ/g, which is 2.75 times greater than hydrocarbon fuels [5,6,7].

This article analyzes the potential for integrated systems in the power market in response to the critical need for a cleaner energy technology and environmental depollution. It is shown that renewable energy must be encouraged, promoted, implemented and demonstrated by full-scale plan especially for use in rural areas. For hydrogen production, the actual biomass processing technologies include: gasification, pyrolysis, reforming, et all [8]. From those, the biomass pyrolysis is the cheapest and simplest method for conversion into energy. The pyrolysis is the thermo-chemical decomposition of biomass under anaerobic environment conditions. Also, pyrolysis is a previous step to other thermo-chemical conversion processes, such as gasification and combustion. Several non-conventional biomass sources have been indicated as promising option for its direct use as fuels, such as hydrogen, that can be obtained through pyrolysis or gasification process. In

this study, as rapeseed, rapeseed cake, and rapeseed meal had been tested for H₂ production by biomass pyrolysis.

2. ENERGY FROM WASTE

All measures taken to maximize the use of high efficiency generation plants and renewable energy sources are important for the increasing the overall level of energy efficiency. Worldwide, the view on waste has changed and in recent years waste is seen as a source of substitution for increasing demand for energy (Figure 1) [1,3]. The way from the initial concept to the obtaining of the first kilowatt of power is not short and has a lot of challenges.

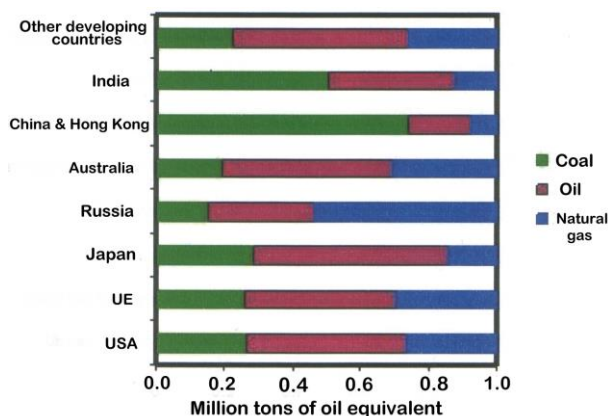


Figure 1. Global fossil fuel consumption.

When considering the demand and opportunity in marketplace of our today's the important points are: the demand for renewable energy is not going to go away, the diminishing of the fossil fuel sources, the needs for new clean technologies that can decrease carbon dioxide amount released into environment. Within the waste to renewable energy sector, there is a hesitancy to invest in projects not supported by an adequate independent technology, without a reference plant, preferably at scale. The people would benefit from pollution reduction, climate mitigation, and the increased trading opportunities that could come from the use of renewable energy sources such as biomass and wastes [9,10]. The aim of any modern biomass energy systems must be to maximize yields with minimum inputs and to use a selection of adequate plant materials and processes. Combined heat and power (CHP) systems are quite common in greenhouses, which grow e.g., salad vegetables, pot plants, etc. Scientific assumptions for a short-term strategy highlight that the most efficient and economically way to replace the thermal plants is to update existing power plants for the increasing their efficiency and to improve their performance towards the environment. However, the utilization of wind power and conversion of gas fired CHP plants to

biomass would significantly reduce the dependence on fossil fuels. Although a lack of generating capacity is forecasted on the long-term, the utilization of the renewable energy potential and the possibilities for increasing energy efficiency are sufficient to meet future energy demands on the short-term. It should be noted, at this point, that the public tend to prefer smaller plants in order to reduce waste supply at a distance and transport costs. The need to reduce CO₂ emissions presents a new, additional challenge, difficult even for the richest of countries [11].

3. ENVIRONMENTAL IMPACTS OF RENEWABLE ENERGY TECHNOLOGIES

At present, renewable energy provides only a little fraction of its potential but many studies have repeatedly shown that renewable energy can provide a significant share of future energy needs, even after accounting for potential constraints. In accordance with *REN21 Renewables 2010 Global Status Report*, renewable energy can replace conventional fuels in four distinct areas: hot water/space heating, electricity generation, vehicle fuels, and rural energy services [12-17].

Heating. Solar hot water makes an important contribution to renewable heat in many countries. Most of these systems are installed and meet a portion of the hot water needs. Worldwide, total installed solar water heating systems meet a portion of the water heating needs of over 70 million households. Also, the use of biomass for heating continues to increase as well as direct geothermal for heating is also growing rapidly.

Power generation. Renewable energy provides about 21% of electricity generation worldwide. Renewable power generators are spread across many countries, and wind power alone already provides a significant share of electricity in some areas such as: 15% in the U.S., 40% in the northern Germany, and 49% in Denmark. Some countries get also most of their energy from renewable sources, including Iceland (100%), Norway (97%), Brazil (85%), New Zealand (65%), Austria (62%), and Sweden (55%).

Transport fuels. Renewable biofuels have contributed to a significant decline in oil consumption after 2006. The 93 billion liters of biofuels produced worldwide in 2009 displaced the equivalent of an estimated 68 billion liters of gasoline, equal to about 5% of world gasoline production.

3.1. Types of environmental impacts

The understanding of the environmental impacts associated with the producing of power from renewable sources such as solar, wind, geothermal,

biomass, and hydropower it is very important [14-17]. The exact intensity and type of environment impacts varies and depend on the technology used, the location, and other factors. Different aspects of the environment impact of renewable energy sources could be analyzed, including, among others factors: the air and water emissions, waste generation, noise generation, hazardous materials, land use and global warming emissions. By understanding the potential and current environment problems associated with each renewable energy source, it can takes steps to avoid or minimize these negative impacts. A whole series of factors are favoring the development of the energy sector based on renewable resources, the most important are the increasing social awareness of the need to limit emissions of toxic substances and greenhouse gases, limiting rising costs of energy from conventional sources and the need to ensure energy security. Because the environment performance of renewable energy systems is greatly improved by an increased efficiency and long lifetimes, both should be improved for whole systems. A brief comparison between environment benefits and costs of the use of different types of renewable energy sources is shown in the Fig.2(1) and Table 1.

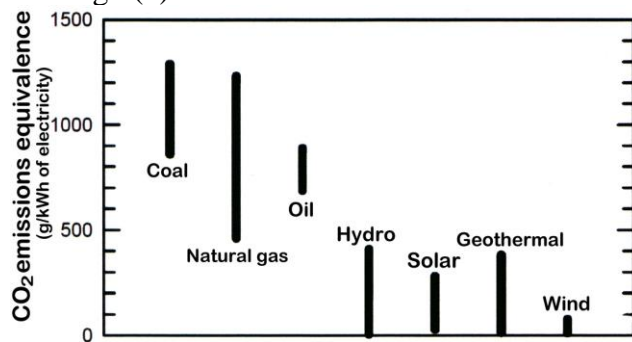


Figure 2. Relative quantities of greenhouse gas emissions from different types of power generation methods, data expressed as CO₂ equivalents [1]

Table 1: Comparison between environmental benefits and costs

Environmental benefits	Environmental costs
1. Energy produced by the renewable energy systems 2. Greenhouse gas savings	1. Production of devices and BOS <input type="checkbox"/> Greenhouse gas emissions <input type="checkbox"/> Heavy metals emissions <input type="checkbox"/> Energy used (Energy pay-back time ¹) 2. Wastes generated by different RES industry

¹Energy Payback Time - EPBT is the time necessary for a system to generate the energy equivalent to that used to produce it.

3.2. Environmental Impacts of Different Technologies

Various technologies based on renewable energy sources have an environmental impact and refer to : environmental impact of wind power; environmental impact of solar power; environmental impact of

geothermal energy; environmental impacts of biomass; environmental impact of hydroelectric power. For exemple ,biomass power plants have some similarities with fossil fuel power plants because both involve the combustion of a feedstock to generate energy. Thus, biomass plants raise some similar issues, but not identical, regarding to air emissions and water use as fossil fuel plants. Biomass power plants, like fossil coal and natural gas fired power plants, require water for cooling and land use impact from biomass power production are influenced by the type of feedstock (either a waste stream or an energy crop that is grown for generating energy) [18,19,20]. The global warming emissions are associated with growing and harvesting of biomass, transporting biomass feedstock to the power plant, and the burning or gasifying the biomass feedstock. Transportation and combustion emissions are same equivalent for all types of biomass. However, global warming emissions coming from the sourcing of biomass feedstock vary widely enough, although it was believed that biomass had net zero global warming emissions, because the biomass in growing absorbed an equal amount of carbon dioxide as the amount released through its combustion, but now it is understood that some biomass feedstock sources are associated with substantial global warming emissions, because it impossible to absorb the entire amount of carbon dioxide released during harvesting, compacting and transport[21,22]. Beneficial biomass resources include energy crops that do not compete with food crops for land, portions of crop residues such as wheat straw or corn stover, sustainably harvested wood and forest residues, and clean municipal and industrial wastes [10,16, 23-25].

4. EXPERIMENTAL PROCEDURE

4.1. Non-conventional biomass sources and sample preparation: The biomass used was rapeseed (*Brassica napus* L.) obtained from the local area. Prior to use, rapeseed was separated and cleaned from other flora and then stored on dry floor at ambient temperature. The production of rapeseed meal requires a process of drying, bleaching, fat extraction and grinding while the rapeseed only requires the drying process, reducing considerably the cost and energy used in the whole process. However, it is expected than the hydrogen production using rapeseed meal will be greater than the rapeseed. Therefore, in this study a high-energy ball-milling pre-process was applied to the rapeseed. High-energy ball-milling generates physical and chemical transformations of substances induced by mechanical

energy [18]. The high-energy ball-milling treatment was carried out in air in a planetary ball mill (Fritsch Pulverisette), vials (250 ml) and balls (9 of 2 cm) of stainless steel grinding materials were used. A 400 rpm rotation rate and a weight ratio of 1:50 sample: milling balls (5.5 g: 250 g) were used. The grinding times tested were 2 min to 20 min.

There are several methods to release amino acids and reducing sugars from seed one of the most used method is the acid hydrolysis [10]. Rapeseed was subjected to acid hydrolysis, and then was tested for hydrogen production by pyrolysis process. Also, after the rapeseed oil extraction results a residue, known as rapeseed cake, which has also undergone the pyrolysis process to obtain hydrogen-rich gas.

4.2. Pyrolysis and hydrogen quantification

The biomass pyrolysis process was performed in an electric furnace and porcelain crucible was used to place 5.0 g of biomass. The porcelain crucible was put into a quartz tube (55 mm of internal diameter) of the electric tubular furnace in a horizontal position. A stream of argon gas was fed through the quartz tube at 50 mL/min. For each test, the system temperature was maintained at 400°C, 450°C and 500°C for 30 min. A scheme of the experimental system used for the pyrolysis tests and hydrogen quantification is presented in Fig. 3.

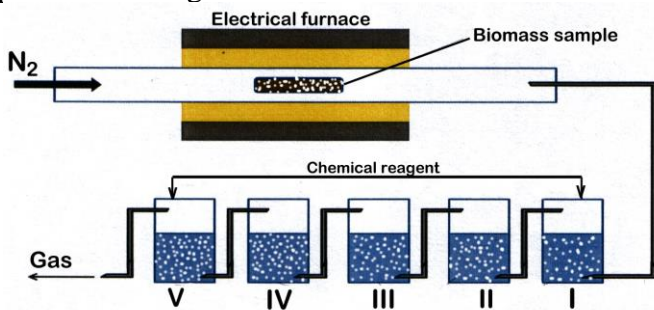


Figure 3. Scheme of the experimental system used for the pyrolysis process and hydrogen quantity quantification.

Hydrogen quantification was carried out using a mixture of acetonitrile (CH₃CN) and sodium acetate (CH₃COONa) as a solvent at a rate of 2 / 100 wt/v using 5 steps connected in series of capture vessels to capture the biomass pyrolysis gas, Fig. 3. The pyrolysis test was done at three temperatures of 450°C, 500°C and 550°C for 30 min. At the end of each pyrolysis time, the reaction medium of each step capture vessel was titrated with 0.1 M NaOH solution and phenolphthalein as indicator to establish the quantity of hydrogen production.

The quantity of hydrogen was evaluated by titration of sodium acetate (CH₃COONa) with sodium hydroxide (NaOH), the acid is generated by the reaction between the molecular hydrogen (H₂)

generated during the pyrolysis process and the sodium acetate, according to Eq.(1):



The titration was performed with 0.1M NaOH solution and the moles of atomic hydrogen resulted were determined with Eq. (2):

$$n_{\text{NaOH}} = n_{\text{H}} = \frac{V_{\text{NaOH}}}{M_{\text{NaOH}}} \quad (2)$$

where n_{NaOH} and n_{H} are the number of moles of NaOH and hydrogen, while V_{NaOH} and M_{NaOH} represents the volume and concentration of NaOH used in the titration step. From number of moles and using the molecular weight of hydrogen, the produced H₂ mass could be estimated.

4.3. Characterization techniques

The morphology and characteristics of the surface of the samples were observed by Scanning Electron Microscopy using a Jeol JSM-6390 LV. X-ray powder diffraction (XRPD) patterns were collected in air and at ambient temperature in a Bruker D-8 Advance diffractometer with Cu K α radiation. Thermogravimetric (TGA) and differential thermal analysis (DTA) were performed using a Perkin Elmer STA 6000 simultaneous thermal analyzer, with inert N₂ atmosphere and a temperature range between 30°C and 750°C at 10°/min.

Reapseed ball-milled samples were analyzed for the reducing sugar content and this was done with the DNS (acid dinitrosalicilic) technique [10,26,27]. Using glucose as a standard, the color intensities were measured at 540 nm and the acid hydrolysis was done in rapeseed to compare the reducing sugar concentration obtained through ball-milling technique. Thermogravimetric (TGA) and differential thermal analysis (DTA) were performed using a Perkin Elmer STA 6000 analyzer, with inert N₂ atmosphere and a temperature range between 30°C and 750°C at 10°/min.

5. RESULTS AND DISCUSSION

As mentioned above, the production of rapeseed, rapeseed cake and rapeseed meal can be used to obtain gas rich in hydrogen by pyrolysis process. However, nothings is known about the effect of particle size and reducing sugar concentration on the process. Therefore, in this study the production of hydrogen from pyrolysis of rapeseed with different modification was studied and analyzed: rapeseed (dried seeds), rapeseed oilcake and rapeseed meal processed by a high-energy ball-milling (Fig.4a,b,c). Scanning Electron Microscopy images (SEM) of rapeseed, rapeseed meal and rapeseed ball milled are

shown in Fig. 5. The rapeseed , rapeseed oil cake extruded are much bigger than the rapeseed meal. It could be seen that the acid hydrolysis treatment performed during the rapeseed meal process decreased the ductility in the material.



Figure 4. Biomass samples: (a)-rapeseeds ; rapeseed meal; (c) rapeseed oil cake extruded ;(d) milled rapeseed oil cake;

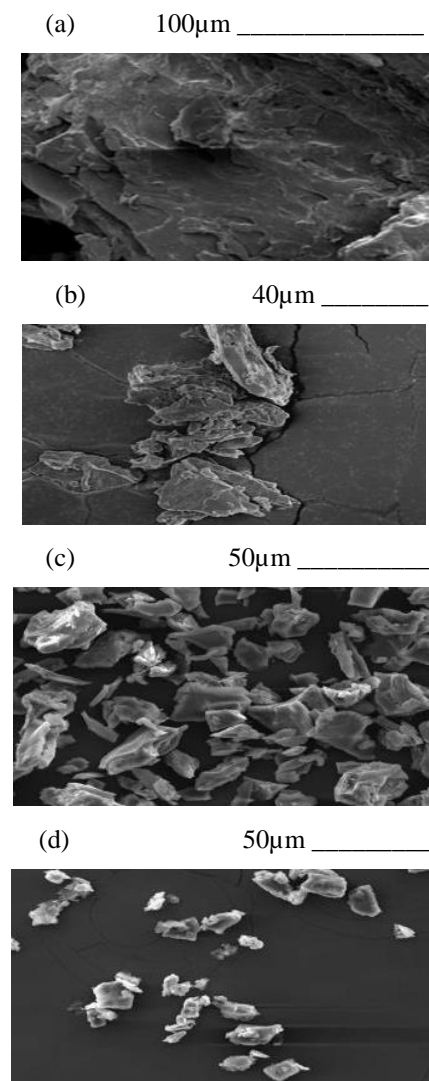


Figure 5. Scanning electron micrographs (SEM) of (a) rapeseed, (b) rapeseed meal, (c) rapeseed ball-milled 2 min, (d) rapeseed ball-milled 20 min.

Flat surfaces are associated with fragile fractures ,while ball milled rapeseed showed different microstructure depending on milling time, Fig.5(c, d). High-energy ball-milling determines physical and chemical modifications of biomass materials induced by mechanical energy and in simple systems the effect is well documented [15, 16, 28,29, 30]. One of the early uses of ball-milling process was reduce the size particle. In Fig.5 (c, d) a clearly rapeseed particle size reduction is observed as a consequence of milling time. After 2 min of milling the average particle size is bigger than 2 μm , while at 20 min it decrease below the 2 μm . X-ray diffraction of patterns of rapeseed meal, rapeseed and rapeseed ball-milled (2 and 20 min) are shown in Fig. 6. On these samples, a typical diffraction of an amorphous material was observed and this behaviour was expected since the rapeseed composition is mainly formed of protein, carbohydrate, oil and moisture. However, after 20 min of milling time the reflection around 20° looks like it is sharpening, this may represent a local ordering, and as a consequence further milling time is required to adjust it.

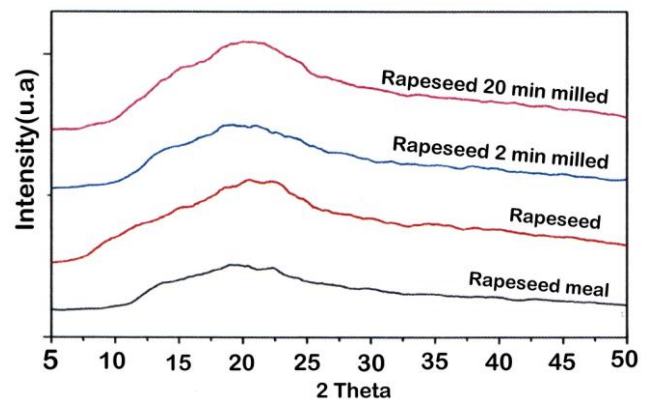


Figure 6. X-ray diffraction patterns of rapeseed, rapeseed , rapeseed ball-milled (2 and 20 min).

The other important point that must be take in consideration is the reducing sugar content from biomass samples [31, 32]. The reducing of sugar concentration from rapeseed (RS), rapeseed meal (RSM), acid hydrolysis rapeseed (RSH), acid hydrolysis rapeseed meal (RSMH), rapeseed ball milled (RS2' and RS20'), as well as rapeseed oil cake (RSOC) are shown in Fig.7. As expected, the reducing sugar content in rapeseed meal (RSM) was higher than in rapeseed (RS) as a consequence of the leaching, extraction of fat and grinding process involved. Additional acid hydrolysis breaks further the rapeseed increasing further the reducing of sugar content, almost double in both situations. However, with just 2 min of high-energy ball-milling time the content of reducing sugar in the sample (RS2') is similar than the content in the acid

hydrolysis rapeseed (RSH) sample. This shows that after 2 min of milling, using balls of 20 mm of stainless steel, it was released almost the same quantity of reducing sugar that could be obtained with 1 h of acid hydrolysis time.

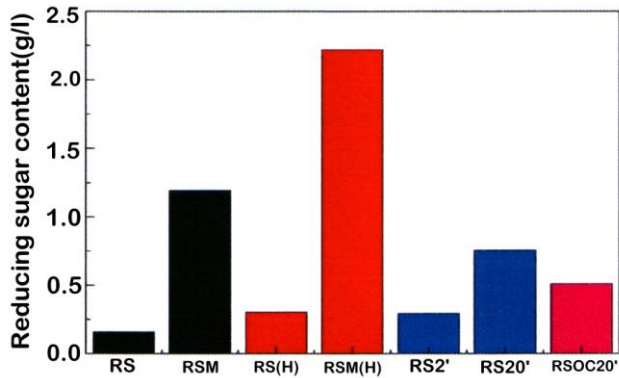


Figure 7. Reducing sugar concentration from rapeseed (RS); rapeseed meal (RSM); acid hydrolysis rapeseed (RS(H)); acid hydrolysis rapeseed meal (RSM(H)); rapeseed ball-milled for 2 (RS2') and 20 (RS20') min); and rapeseed oil cake ball-milled 20 min (RSOC20').

After 20 min of milling (RS20') the content increased more than four times comparing with rapeseed, this demonstrates that high-energy ball-milling could be a suitable, easy and low cost alternative technique to decrease the sugar content. Based on the thermal behaviour of rapeseed, three temperatures were chosen to evaluate the hydrogen production from biomass pyrolysis: 400°C, 450°C and 500°C. The selection was done considering the main degradation region resulted from TGA analysis. The hydrogen amount resulted from pyrolysis experiments are shown in Fig.8.

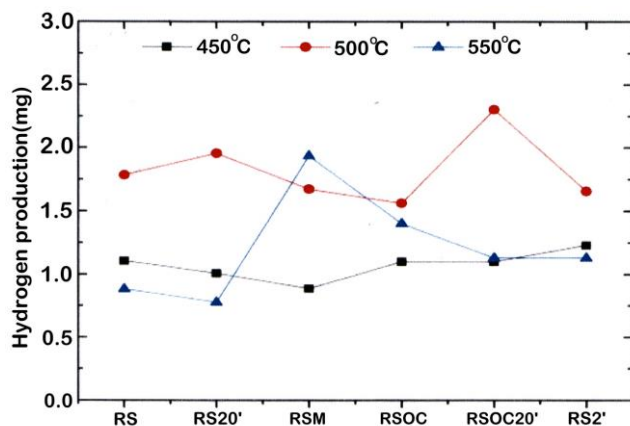


Figure 8. Hydrogen production from pyrolysis tests at different temperatures of: rapeseed (RS); rapeseed meal (RSM); rapeseed ball-milled for 2 (RS2') and 20 (RS20') min); rapeseed oil cake (RSOC); and rapeseed oil cake ball-milled for 20 min (RSOC20').

The results show that the pyrolysis process depends on particle size but does not depend too much of reducing sugar content. The production at 450°C is almost similar in all the samples, around 1.2 mg of

hydrogen. At 500°C, the production increase and then drop at 550°C. It can say that the process depends much more on the temperature selection rather than biomass microstructure. Finally, this study shows that hydrogen can be obtained from waste biomass pyrolysis process easily and at low cost.

6. CONCLUSION

Each of the renewable energy technologies is in a different stage of research, development and commercialization and all have differences in current and future expected costs, current industrial base, resource availability and potential impact on energy supply. The future energy use and consequent environmental impacts (acid precipitation, ozone depletion and the greenhouse effect or global warming) are comprehensively related to the energy source used. Throughout the theme, several issues relating to renewable energies, environment and sustainable development were examined from both current and future perspectives. The experimental results show that it is possible to obtain hydrogen from biomass pyrolysis. The microstructure or reducing sugar content does not seem to have a determinant effect on hydrogen yield released from biomass pyrolysis process. Thus, hydrogen can be obtained from biomass conversion at low cost. Rapeseed thermal stability was increased during the ball-milling process and this demonstrates that high-energy ball-milling could be a good, easy and low cost method to increase reducing sugar content, this can be very useful for example, to produce culture media.

7. ACKNOWLEDGEMENTS

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