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Production of Hydrogen from Pyrolysis of Biomass: Influence of Temperature, Substrate and Catalyst

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Abstract: Like hydrogen is an energy vector, its production is a research orientation very interest among these axes. The pyrolysis technique is especially interesting that attached great importance to the problems of pollution and to environment. Not forgetting of course the gas obtained (rich in hydrogen) that can be used and valued. The goal is to increase the volume of hydrogen in this gas obtained why several experiments were conducted to study the influence of temperature, substrate and catalyst on the volume of hydrogen produced.

Key words: Biomass, pyrolysis, gasification, bio-hydrogen, valued, orientation, Algerie

INTRODUCTION

Hydrogen can be produced from a variety of feedstock. These include fossil resources such as natural gas and coal as well as renewable resources such as biomass and water with input from renewable energy sources (e.g., sunlight, wind, wave or hydro-power). A variety of process technologies can be used including chemical, biological, electrolytic, photolytic and thermo-chemical. Each technology is in a different stage of development and each offers unique opportunities, benefits and challenges. Local availability of feedstock, the maturity of the technology, market applications and demand, policy issues and costs will all influence the choice and timing of the various options for hydrogen production.

An overview of the various feedstock and process technologies is shown in Fig. 1. Several technologies are already available in the marketplace for the industrial production of hydrogen. The first commercial technology, dating from the late 1920 was the electrolysis of water to produce pure hydrogen.

In the 1960, the industrial production of hydrogen shifted slowly towards a fossil-based feedstock which is

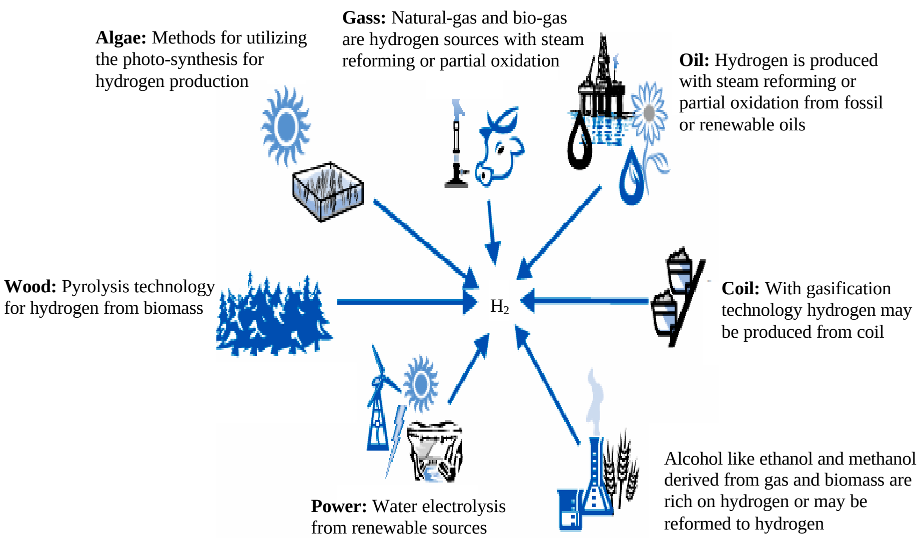

Fig. 1: Some feedstock and process alternatives

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the main source for hydrogen production today. In biomass conversion processes, a hydrogen-containing gas is normally produced from pyrolysis. Pyrolysis is one of the most promising thermo-chemical conversion routes to recover energy from biomass.

During pyrolysis, biomass is thermally decomposed to solid charcoal, liquid oil and H_2-rich gases under an oxygen absence condition. The yields of end products of pyrolysis and the composition of gases are dependent on several parameters including temperature, biomass species, particle size, heating rate, operating pressure and reactor configuration as well as the extraneous addition of catalysts (Demirbas and Arin, 2002; Bridgwater, 1994).

Temperature and residence time as the 2 most important parameters have been investigated widely in bench scale reactors including fixed beds (Ates *et al*., 2005) fluidized beds (Chen *et al*., 2004) and others (Li *et al*., 2004). Generally, H_2-rich gas products are favored at a high temperature and long residence time (Yang *et al*., 2006).

MATERIALS AND METHODS

Several experiments were performed to study the influence of some parameters like the temperature, type of biomass and catalyst on the volume of hydrogen contained in gas obtained from pyrolysis.

Pyrolysis yields: The yields and composition of the pyrolysis products depend on the operation conditions. Figure 2a-c shows the evolution of the gas, liquid and solid fraction yields with the pyrolysis temperature.

As reported by other researchers working with similar types of waste (Rumphorst and Ringel, 1994) an increase in the final pyrolysis temperature gives rise to a decrease in the solid fraction and to an increase in the gas fraction. The liquid fraction, increases slightly when the end temperature is increased from 450-650°C but remains more or less constant above 650°C. The effect of the heating rate is only important at low end temperatures (i.e., 450°C).

Thus at this temperature the higher the heating rate, the more efficient the pyrolysis is resulting in a higher production of liquids and gases and a decrease in solid residue. At temperatures >650°C, this effect is practically negligible.

The gas fraction: In the study, the researchers are interesting by the fraction specially hydrogen fraction.

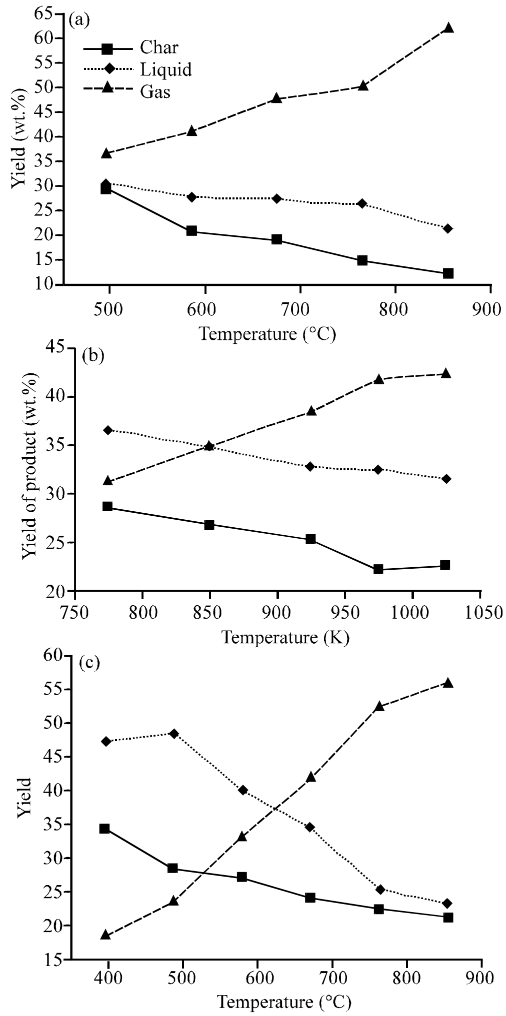

Fig. 2: Effect of temperature on pyrolysis products yields; a (Yang *et al*., 2006), b and c (Encinar *et al*., 2008)

RESULTS AND DISCUSSION

Temperature effect: Analyses of the composition of the gaseous products of pyrolysis have shown that CO_2, CO, H_2, O_2, N_2 and C_xH_y are the main components released during pyrolysis (Fig. 3a-c). At the lower temperature (250-350°C), CO_2 is the dominant gaseous species, although N_2 is also present. Increasing the pyrolysis temperature lead to a decrease in CO_2 and to an increase in CO and H_2 over the whole range temperatures studied in this research. On the other hand, the hydrocarbons CH_4, C_2H_4 and C_2H_6 show a maximum in their yields at around 600°C for CH_4 and 450°C for C_2H_4 and C_2H_6. Although, the temperatures at which the gases reach a maximum are practically the same for both heating rates, some quantitative differences can be observed. Thus for any pyrolysis temperature.

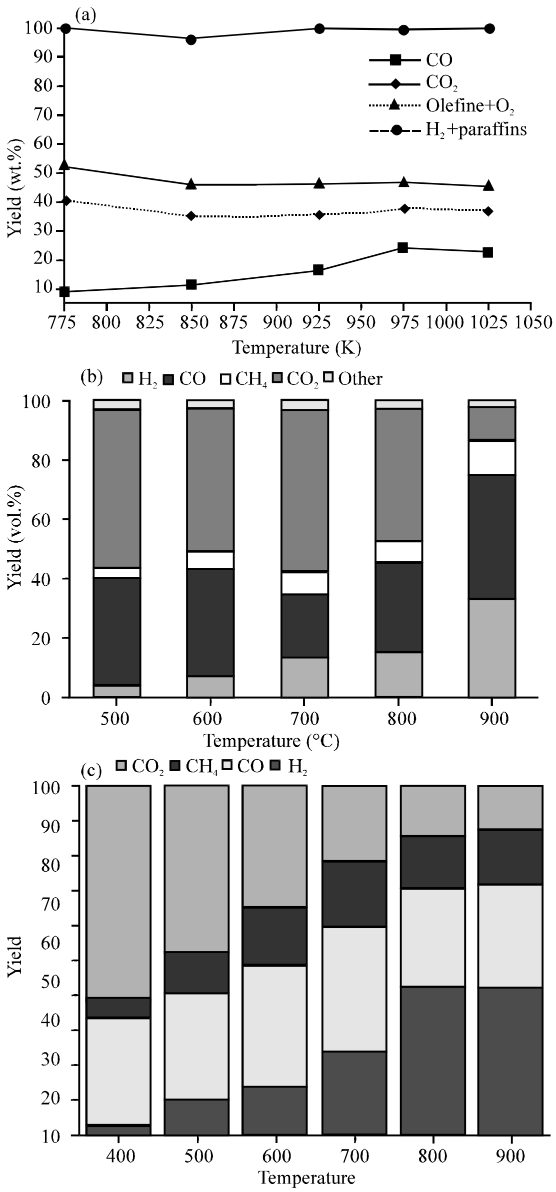

Fig. 3: Effect of temperature on hydrogen gaz obtaining; a) (Caglar and Demirbas, 2002); b) (Yang *et al*., 2006) and c) (Encinar *et al*., 2008)

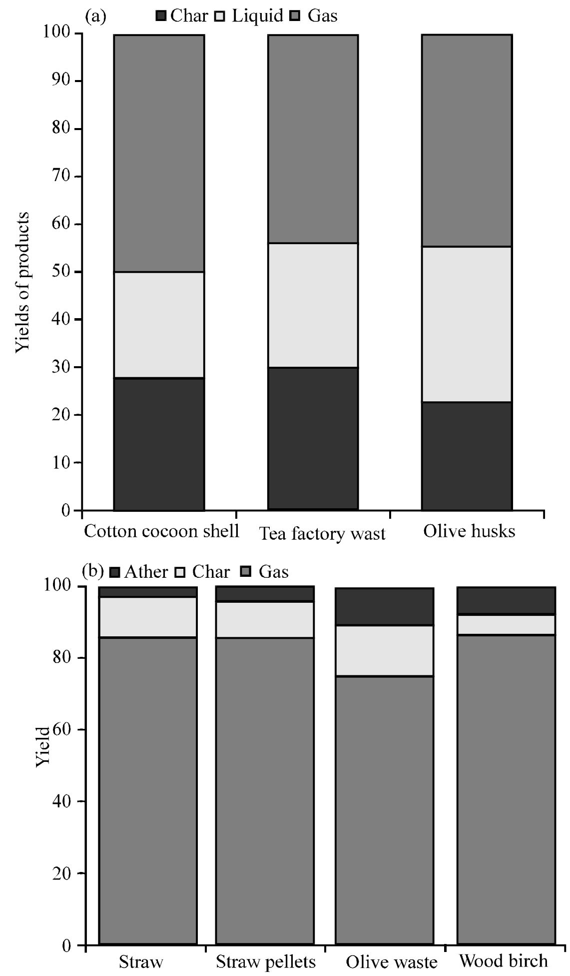

Fig. 4: Effect of type of biomass on products yield; a) (Demirbas, 2001) and b (Zanzi *et al*., 2002)

Table 1: Elemental compositions of biomass samples (Demirbas, 2002)

Parameters	C	H	O	N
Olive husk	47.4	5.8	36.3	1.4
Cotton cocoon shell	50.2	5.8	42.7	1.3
Tea factory waste	49.6	5.1	42.6	2.7

Effect of type of biomass: The type of biomass effect on products yield in this study researchers are interesting by the type who gives us the maximum of hydrogen. Demirbas use 3 types of biomasse (cotton cocoon shell, tea factory waste and olive husk), it can be shown in Fig. 4a, b then the fraction of gas from pyrolysis of cotton cocoon shell at 1025 K is 50.1 and 44.6 (wt.%) in tea factory waste and only 43.7 (wt.%) in olive husk (Demirbas, 2001). Now the volume of hydrogen in gas; Fig. 5a, b shows the volume of hydrogen obtaining from the 3 types at 1025 K. Researchers notice then with olive husk the volume of hydrogen arrive at 54.5 and 50% with tea factory waste and only 44.4% with cotton cocoon shell. So, it cannot conclude then more gas give more hydrogen. So, now the relation between elemental compositions and volume of hydrogen obtaining. Table 1 shows the element composition of the 3 types of biomass.

Effect of catalyst on hydrogen yield: A catalyst decreases the activation energy of a chemical reaction. Catalysts participate in reactions but are neither reactants nor

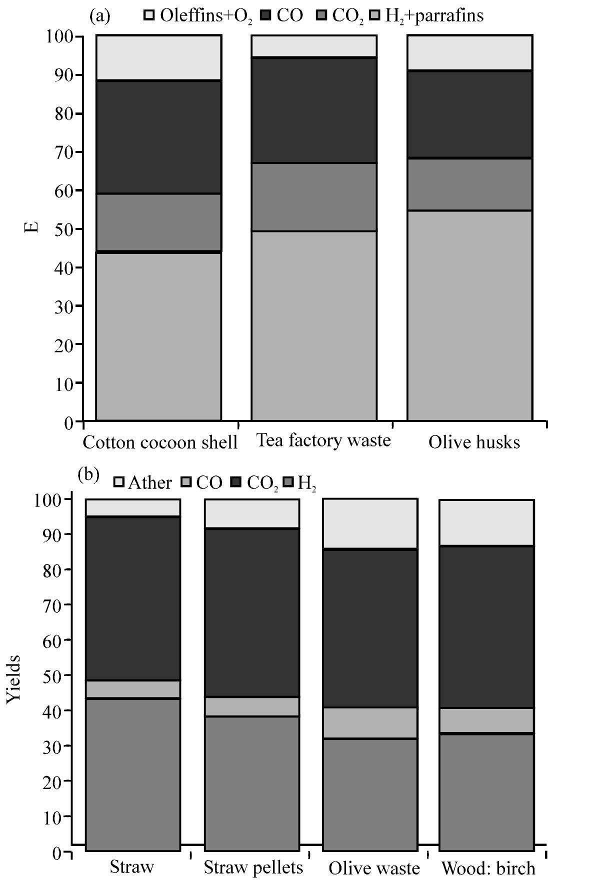

Fig. 5: The distributions of gas products; a) (Demirbas, 2001) and b) (Zanzi *et al*., 2002)

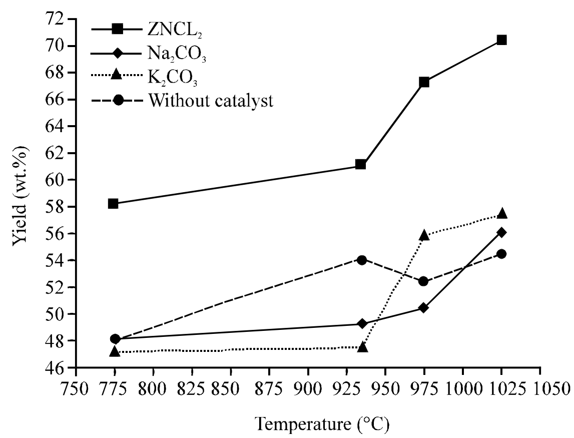

Fig. 6: Effect of catalysts on hydrogen gas obtaining (Demirbas, 2001)

products of the reaction they catalyze. An exception is the process of autocatalysis where the product of a reaction helps to accelerate the same reaction. Researchers research by providing an alternative pathway for the reaction to occur thus reducing the activation energy and increasing the reaction rate. In the study, there are used the results. Demirbas (2002). There is used 3 catalysts ($ZnCl_2$, K_2CO_3 and $NaCO_3$). Figure 5b shows the evolution of hydrogen following the increase in temperature. The largest hydrogen-rich gaz yield obtained from olive husk using $ZnCl_2$ as catalyst at bout 1025 K temperature is 70.3; in general in the pyrolysis biomass the yield of hydrogen-rich gas product increase with $ZnCl_2$ catalyst (Fig. 6). The effect of K_2CO_3 and Na_2CO_3 as catalysts on pyrolysis depend on the biomass species.

CONCLUSION

An increase in the final pyrolysis temperature of biomass studied gives rise to a decrease in the solid fraction and to an increase in the gas fraction while the liquid fraction remains almost constant. From an energy point of view more gas gives to us more hydrogen. At low temperatures as the heating rate increases, cracking reactions are favored giving rise to a higher concentration of light compounds in the pyrolysis oils. At temperatures above 650°C, the effect of the heating rate is not as noticeable because at these temperatures the decarbonylation of oxygenated hydrocarbons.

Predominates over cracking reactions. For use as fuels the organic fraction of the liquid pyrolysis products has heating values that are comparable to some conventional fuels. The potential that these products have for use as fuel is therefore high. There is a clear dependence of the release of hydrocarbons on the heating value this reaches a maximum at those temperatures at which the concentration of hydrocarbons in the gaseous stream is maximum. The high average heating values which are comparable to those of some fuels together with the maximum values. The powered catalyst is $ZnCl_2$ with him obtained 70.3 wt.%. So to obtaining more hydrogen in gaz we must to increase. Temperature use the biomass and used $ZnCL_2$ as catalyt.

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