APPLICATIONS OF THE THERMOCHEMICAL TREATMENTS IN THE SUSTAINABLE DEVELOPMENT CONTEX

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Abstract. Over the last years, many researchers have investigated how renewable energies can contribute to the security of the energy supply. On the other hand, soil decontamination technologies are another interesting topic related to environmental protection. In the first part of the paper, we illustrate some results obtained by a PhD thesis prepared at the "POLITEHNICA" University of Bucharest on pyrolysis thermal treatments of the biomass. The last part of the paper is dedicated to a new research began in the framework of the project co-financed by RECOLAND European funds (ID519, SMIS-CSNR: 11982, Nb. 182/18.06.2010). It is about contaminated soils pyrolysis and potential human health risk before and after the thermal treatment used as decontamination method. We have to underline that RECOLAND takes into consideration, besides soils pyrolysis, also incineration, biological and electrochemical treatments and cost analysis. This way, the multicriteria decisional system that will be developed will be able to decide which remediation technique is most appropriate to be applied in order to decontaminate the soil.

Introduction

Difficulties for the energy-supply (primary energy demands increase as emissions do) require technical progress and capital provision, and creates possibilities of decreasing the environmental impact and of ensuring the sustainability of the dynamic system (Intergovernmental Panel on Climate Change, 2007).

Energy is considered an essential factor for economical and social development. There are different ways to store, convert and amplify energy abundance for our use. Energy sources play and will play an important role in the world's future.

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Among the existent thermal technologies, the present paper refers to pyrolysis. It is defined as a treatment that takes place at a slow heating rate. It is recognized as the process with the biggest char yield. Biomass pyrolysis has been practiced for centuries in the manufacture of charcoal, but the physical and chemical processes occurring during pyrolysis were investigated only recently.

The use of biomass products provides substantial benefits as far as the environmental impact is concerned. Biomass absorbs carbon dioxide during growth and releases it during combustion. Therefore, biomass helps the atmospheric carbon dioxide recycling and does not contribute to the greenhouse effect (Chaurasia et al., 2007). Biomass has either been processed to increase its energy content or burned directly in furnaces. Thermal processes such as pyrolysis, gasification, anaerobic digestion and alcohol production have been widely applied to biomass in order to increase its energy content. Energy produced from biomass or its conversion products represents an important part among the most used energy sources in the last period. Because biomass is a renewable energy source, it is abundant and it has domestic usage too, it can contribute to solve an important problem of the world: the reduction of the conventional fuel usage (petroleum products, natural gas). Applying some physical, chemical and biological conversion processes, biomass can be transformed into liquid, solid and gaseous fuels (Demirbaş, 2000, 2001). The objective of biomass materials conversion is to transform an organic solid material that is originally difficult to handle, bulky and of low energy concentration into fuels having physical and chemical characteristics that permit economical storage and transferability through pumping systems.

A part of the experimental campaign done at pilot scale for a PhD thesis at the POLITEHNICA University of Bucharest (Bulmău, 2009) is presented in the first part of this paper. The research goal of this PhD thesis was to study the technologies of pyrolysis of wooden biomass for alternative fuels generation. For the considerations presented in the previous paragraph, some experiments of the PhD researches were designed to study the effects of the process temperature on the gases resulted from biomass pyrolysis (qualitative and quantitative analysis). If PhD researches have used pyrolysis in order to produce fuels with thermal-physical-chemical properties inferior to those of conventional fuels, the RECOLAND project intends to employ pyrolysis as a thermal treatment technology applied to contaminated soils. In this project, also other decontamination technologies are studied: incineration, electroremediation and bioremediation.

1. Thermochemical treatment technologies

Various technologies for thermochemical conversion of biomass (i.e. combustion, pyrolysis, gasification) were developed during the last years; the most used technique is still based on combustion. The international policy on the CO_2 emissions forced the industrials from the energy sector to turn to alternative processes of pyrolysis and gasification. In the last decade, many research centers started to reconsider alternative thermal treatment technologies as pyrolysis and gasification applied to biomass for alternative fuels production.

From the industrial point of view, the pyrolysis process presents advantages compared to other thermo-chemical processes, such as a lower operating temperature and inert atmosphere. The first one allows decreasing the well known ash melting problems, while the second one reduces the dioxins and furans formation. Obviously, it is necessary to talk about the disadvantages: the most critical one is the endothermic character of this process (Aranzo, 2008). In spite of this requirement of energy, quite critical at the present, pyrolysis is still a good industrial option for the waste treatment.

2. Technologies for biomass pyrolysis

In the experimental section of the PhD thesis, an important part was dedicated to wooden biomass pyrolysis processes. The experiments were conducted in a tubular reactor (NABERTHERM) – RO 60/750/13 model (fig. 1). It is used in the Laboratory of Environmental and Renewable Energy Sources, of the POLITEHNICA University of Bucharest (Power Engineering Faculty) and it operates discontinuously. The pyrolysis reactor has a horizontal position and it is used to study the thermal degradation processes of the organic solids at pilot scale. The electrical furnace is optimal for the application of the discontinuously mode treatments.

The fixed bed furnace diagram is presented in the figure below:

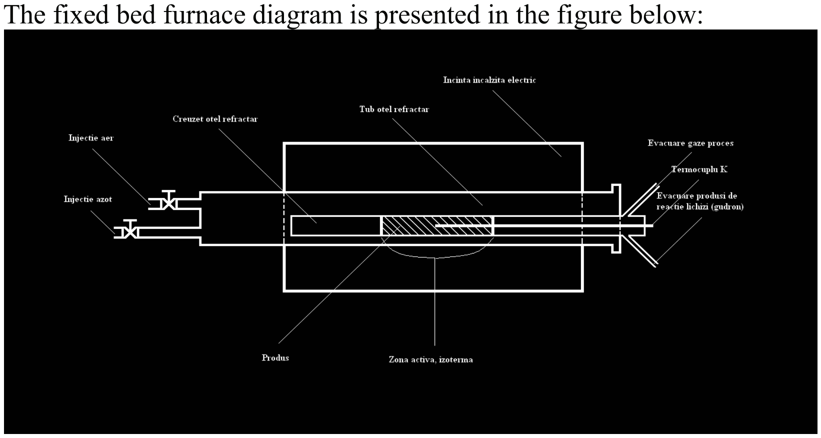

Fig. 1 - Diagram of the horizontal electrical furnace

The temperature range for the reactor is 20 – 1300°C. This furnace has a temperature inspecting frame that offers the possibility to set the process temperature, the process work time (stationary time of the sample in the furnace at the process temperature) and the heating rate. While the pyrolysis process took place, a nitrogen flow was inserted inside the reactor assuring an inert atmosphere. This was measured using a rotameter.

For the thermo-chemical treatments, the analyzed material was cherry sawdust. It was treated at different pyrolysis temperatures: 450 °C, 600 °C, and respectively 800 °C for a stationary time of 30 minutes. For all the pyrolysis processes, the sample mass was of 25g. Every sample of sawdust has been placed in a refractory steel crucible with a parallelepiped form 100 cm long, 4 cm wide and 3 cm high.

3. Results

3.1. Temperature influence on components of the pyrolysis gases. In order to determine the temperature influence, qualitative and quantitative analyses were carried out using a Schimadzu GCMS-QP 2010 Plus. This was linked to the pyrolysis tubular reactor. For measurements, the carrier gas was He with a purity of 99.995% and a flow rate of 0,1 ml/min. The separations were performed on a GC Carbon Plot column US 084124 J (30.0 m x 0.32 mm i.d x 1.5 µm; Agilent Technologies). The injection was realized by a VICI Valco Instruments Co. Inc. valve with 2 positions and 6 entries.

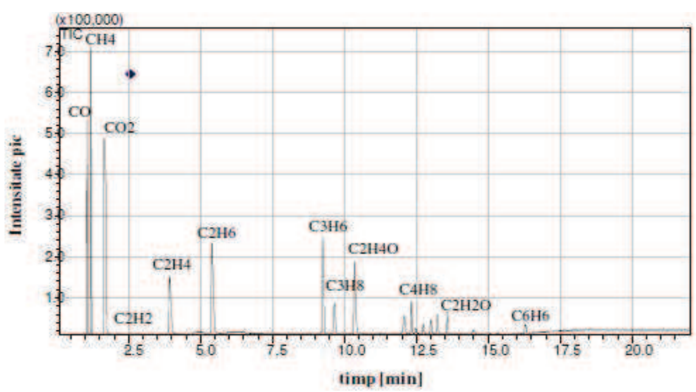

Fig. 2 - Chromatogram of the gases resulted from pyrolysis at 600°C (*Bulmău, 2009*)

The main components of the pyrolysis gases resulted from the process were: H_2, CO, CH_4, CO_2 and a few hydrocarbons with low molecular mass. Sometimes, paths of O_2 and N_2 were identified. These could result from biomass decomposition or can be emanated by the air absorbed by the installation. It should be noted that the carrier gas was not N_2. Figure 2 presents the chromatogram of the cherry wood pyrolysis produced at 600°C. All the chromatograms for the pyrolysis processes at the above mentioned temperatures (450°C, 600°C respectively 800°C) were done.

Tab. 1 **-** Composition of the pyrogases of pyrolysis done at 450°C

Pyrogases composition	**Concentration [%volume]**
CO_2	45,13
N_2	0,53
CO	17,49
H_2	10,49
CH_4	7,68
O_2	3,1
C_2H_2	2,36
C_2H_6	2,11
C_3H_3	0,04
C_3H_6	2,8
C_3H_8	0,7
C_2H_4O	3,39
1-prophyne-2 methyl	0,87
2-butene	0,92
C_4H_{10}	0,21
Furan	0,33
Propanol	0,18
Acetone	0,65
acetate methyl	0,92
2-butanone	0,02
C_6H_6	0,05
Toluene	0,03
TOTAL	100,00

Source: (*Bulmău, 2009*)

Generally, the maximum concentration of pyrogases is registered after approximately 5 minutes after the process has started. Next, a decreasing concentration follows and it continues till the end of treatment. CO is characterized by the greatest molar concentration, while C_3H_3 and C_3H_8 have the lowest one, not depending on the operating conditions. On the other hand, the concentrations of H_2, CO_2 and CH_4 are strictly depending on the process parameters.

The components of the pyrogases and their percentages obtained at 450°C are presented in Table 1.

3.2. The influence of the temperature on the percentage concentration of the non condensable pyrogases. The influence of the pyrolysis temperature on non condensable pyrogases is shown in figure 3. The level of the concentrations of the main pyrogases components presented in the graphic is the results of the three pyrolysis processes. We can notice that molar concentrations of H_2, CO and CH_4 increase, while temperature is rising. On the other hand, the concentration of CO_2 decreases if the temperature increases. This is due to the CO_2 formation dependence on the O_2 concentration value. Operating conditions necessary to apply the pyrolysis treatments of the wooden biomass have induced a low concentration of O_2 respectively CO_2 in the pyrogases.

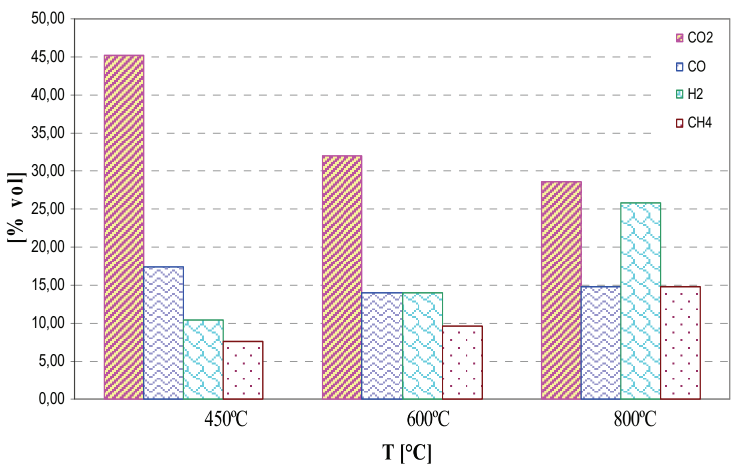

Fig. 3 - Variation of the pyrogases as a function of process temperature (*Bulmău, 2009*)

The reactions of depolymerisation, decarboxylation and thermal cracking are strongly favored by the rising of the process temperature. All these reactions are responsible for the formation of pyrogases species. Hydrogen and methane are formed starting from the reactions of depolymerization and the cracking of the volatile matters, while CO and CO_2 derive from the reactions of decarboxylation and depolymerization (Encinar et al., 2000, Shadizadeh, 1968).

It is well known that H_2 production is favored by high temperatures. This raised efficiency of H_2 generation is due to the reactions between the intermediary products of the pyrolysis (Li et al., 2004). In fact, at high temperatures, it is possible that the dry phase and the pyrolysis phase take place at the same time. The produced water vapors can interact with the intermediary products of the pyrolysis.

The experiments done in our campaign demonstrate the same trend. Consequently, we can notice that the increase of the pyrolysis temperature from 450ºC to 800ºC has determined the raising of the H_2 production by approximately 28%. On the contrary, the CO and CH_4 generation increases more slowly than H_2. At 450ºC, the CH_4 concentration was of 4,92 %, while at a pyrolysis temperature of 800ºC, it has reached 13,92%. For the same temperature interval, the increase of O_2 was of about 5%.

3.3. Pyrolysis technologies for contaminated soils. Technologies of thermal remediation of contaminated soils use heat to separate, destroy or immobilize contaminants. Most of the thermal treatments used for soil decontamination are ex-situ: desorption, vitrification, pyrolysis and incineration.

If the general goal of the biomass pyrolysis is energy production accompanied by a low environmental impact, the polluted soil pyrolysis can be a solution for decontamination, bringing back the clean soils to natural cycle. More than that, an important advantage of this type of polluted soil decontamination is represented by the reduction of the environmental impact and in the same time, of the potential risks to human health.

Pyrolysis technologies seem to be efficient for soils contaminated with organic compounds (e.g. hydrocarbons, creosote, PAH, PCB or dioxins). The pyrolysis is characterized by oxygen absence and by low temperatures and these could transform it into an optimal technology for decontamination of the soil with a high content of organic matter and for waste treatments that do not generate dioxins. Metals may be removed from the soil as a result of the higher temperatures associated with the process, but they are not destroyed. To reduce the cost of the treatments, pyrolysis technologies require drying the soil to achieve a low content of soil moisture (< 1%). Even if the soil thermal treatments are more costly compared to the other remediation technologies, they assure a rapid cleaning of the polluted soils. Starting from the doctoral thesis results, the pyrolysis treatment for soil clean-up will be used. It will be one of the decontamination methods applied for soil clean-up in the research activities of the RECOLAND project. The aim of the treatments is not only to eliminate the toxic and persistent contaminants (e.g. Cd, As, Ni, Pb PCB or PAH) from the soils, but also to characterize the pyrogases composition and to repopulate the solid waste (ash and char) with bacteria. Also, it will be very interesting to study the process temperature influence on the PAH content of pyrogases resulted from contaminated soil treatments.

Conclusions

From the point view of the industrial field and taking into account all the thermal processes, the main advantage of the pyrolysis is the generation of pyro-products that can be used for energy production due to the low temperatures of the process. If the general goal of the biomass pyrolysis is energy production accompanied by a low environmental impact, the polluted soil pyrolysis can be a solution for their decontamination, for their returning to the natural cycle. More than that, an important advantage of this type of polluted soil decontamination is represented by the decrease of the potential environmental impact and in the same time, of the human health risks caused by contaminated lands. Alternatively, pyrolysis technologies seem to be efficient for soils contaminated with organic compounds: PAH, PCB, dioxins and others. Starting from the PhD thesis results, the pyrolysis treatment for soils clean-up will be used, this technology being one of the decontamination methods applied for soil clean-up in the research activities of the RECOLAND project. The aim of the treatments is not only to eliminate the toxic and persistent contaminants (e.g. Cd, As, Ni, Pb PCB or PAH) from the soils, but also to characterize the pyrogases composition and to repopulate the solid waste (ash and char) with bacteria.

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