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Slow, Wet and Catalytic Pyrolysis of Fowl Manure

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***Abstract*—**This work presents the experimental results obtained at a pilot plant which works with a slow, wet and catalytic pyrolysis process of dry fowl manure. This kind of process mainly consists in the cracking of the organic matrix and in the following reaction of carbon with water, which is either already contained in the organic feed or added, to produce carbon monoxide and hydrogen. Reactions are conducted in a rotating reactor maintained at a temperature of 500°C; the required amount of water is about 30% of the dry organic feed. This operation yields a gas containing about 59% (on a volume basis) of hydrogen, 17% of carbon monoxide and other products such as light hydrocarbons (methane, ethane, propane) and carbon monoxide in lesser amounts. The gas coming from the reactor can be used to produce not only electricity, through internal combustion engines, but also heat, through direct combustion in industrial boilers. Furthermore, as the produced gas is devoid of both solid particles and pollutant species (such as dioxins and furans), the process (in this case applied to fowl manure) can be considered as an optimal way for the disposal and the contemporary energetic valorization of organic materials, in such a way that is not damaging to the environment.

***Keywords*—**Brushwood, fowl manure, kenaf, pilot plant, pyrolysis, pyrolysis gas.

I. Introduction

The disposal of large amounts of materials, especially organic ones such as urban and industrial wastes, and the valorization of marginal agricultural lands are two extremely important requirements in technologically developed societies. Besides this, further technological advancement can only be made possible by increasing the availability of low cost energy and reducing environmental impact and carbon dioxide emission into the atmosphere.

In this work we present the results from an experimental-demonstrative plant for the disposal of waste organic materials of any origin with the contemporaneous production of both electrical and thermal energy and with low pollutant emissions; the proposed process is a kind of pyrolysis named "slow, wet and catalytic". Although this was specifically a kind of process characterized by extremely innovative elements, which can be traced back to the adjectives "slow", "wet" and "catalytic", pyrolysis has long been the subject of different studies and applications, even recent ones [1]–[4], considering the wide variety of materials that can be used and the great number of the possible combinations of the process parameters [5].

The demonstrative plant, designed by Maim Engineering srl company and presented in a previous article [6], operates near Cagliari (Sardinia, Italy). It can treat up to 20 kg/h of organic materials producing a fuel gas mainly composed of hydrogen, carbon monoxide and light hydrocarbons. The produced gas can be burned without any damage to the environment, realizing a significant valorization of any organic material, such as fowl manure, which is discussed here.

The size of the available structure does not allow industrial use, because of the small amount of material that can be treated, nevertheless it is fundamental for the demonstration of the potential of the proposed process; furthermore, it is used for experimental purposes in connection with our laboratory equipment, in order to better define all the process parameters (kinetic, fluid dynamic, etc.) necessary to design similar larger sized plants.

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II. Description of the Process

The slow, wet and catalytic pyrolysis process [7] consists in the cracking reactions of the organic bonds, followed mainly by the reaction of organic carbon with water: $C+H_2O \rightarrow CO+H_2$. Secondary reactions also occur, which cause the formation of CO_2, light hydrocarbons and other components, depending on the particular composition of the fed organic material and on the process parameters.

As the reactions that happen during the initial phase of the pyrolysis process are essentially cracking reactions of the biomass, some specific components are added in order to catalyze these reactions. The result is an increase in the amount of obtained pyrolysis gas to the detriment of liquid and solid products; the composition in terms of hydrogen and carbon monoxide is also increased.

The organic material used to feed the plant on this occasion was fowl manure. This choice was guided by the great availability of such a kind of waste material in the local region; furthermore, its disposal is difficult and expensive. The dry material is fed to the reactor (3 in Fig. 1 and 2) by means of a hopper (1 in Fig. 1 and 2) and an Archimedean screw (2 in Fig. 1 and 2), tapered at its end in order to reduce the drag of external air into the reactor as much as possible. As well as the dry fowl manure, water is also fed to reach 30% (in weight) of the dry fowl manure. A heating jacket (4 in Fig. 1 and 2), was installed coaxial to the reactor and a hot gas, burned at about 700°C, flows in the interspace between the reactor and heating

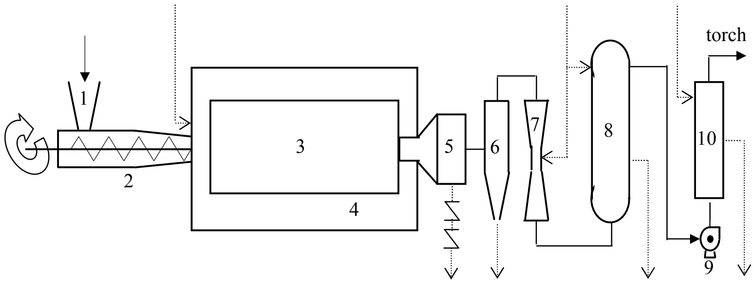

Fig. 1 Schematic representation of the process (— process lines; ··· water and solids auxiliary lines; 1: hopper; 2: Archimedean screw; 3: reactor; 4: heating jacket; 5: solid separation system; 6: cyclone; 7: adiabatic quench; 8: wet scrubber; 9: side channel blower; 10: flow device)

Fig. 2 Photographic views of the pilot plant (numbers are the same as Fig. 1)

jacket; this gas is produced during the plant starting up phase by LPG burners. The reactor internal temperature is maintained at a constant temperature near 500°C by a control system that regulates the flow rate of the gas sent to the burners. The pyrolysis gas coming from the reactor passes through an area of calm, where most of the inert particles and biochar are separated and discharged by means of a double dump valve (system 5 in Fig. 1 and 2). Then the gas is sent to a cyclone separator (6 in Fig. 1 and 2) where the residual solids are separated, after which it is cooled with water by an adiabatic quench system (apparatus 7 in Fig. 1) and purified into a wet scrubber (8 in Fig. 1 and 2); finally, after having passed through a flow device (10 in Fig. 1 and 2), the produced gas comes out to be burned. The conveying of the pyrolysis gas is made by a side channel blower (9 in Fig. 1 and 2) positioned in the process line between the scrubber and the flow device; it is regulated in such a way that the reactor is maintained with a slight depression (3-5 mm of water column).

The reactor is made of stainless steel (AISI 316L), resistant to high temperatures, with an internal diameter of 0.40 m and a length of 1.0 m; it is made to rotate around its axis, which has an angle of 2° to the horizontal, at a rate of one round per minute. The thus configured structure allows a feed material residence time of about 1.5 hours. The internal reaction chamber is coaxial to another tube with a diameter of 1.0 m, inside which there is a layer of refractory bricks and a layer of rock wool, with a total thickness of 20 cm. The lower part of this tube houses the burner nozzles (which are fed with LPG during the starting up phase and with a part of the produced pyrolysis gas during the operation in the steady state) in order to provide the heat for the pyrolysis reactions to occur.

The hot washing waters (at about 40°C) coming from the wet scrubber contain the residual solids and they are consequently sent to a decanter, where the hot clarified water and the solids are separated. The sludges are removed from the bottom of the decanter and recirculated directly to the reactor loading hopper. The gas coming from the washing section is further deprived of solid and liquid particles by making it pass through a gravel filter before being conveyed to the flow device by the blower. A part of the produced gas is used to meet the energy consumption of the process itself.

III. Experimental

The core of the process is represented by the reactor, in which the organic material, mainly composed of combined carbon and hydrogen, together with other components in smaller amounts (nitrogen, oxygen, chlorine, sulphur), is transformed into gaseous components, namely molecular hydrogen and carbon monoxide; also minor quantities of carbon dioxide and light hydrocarbons (CH_4, C_2H_6, C_3H_8), as well as very small amounts of hydrides, are produced.

During this first stage, experimentation was carried out in order to study the composition and amounts of the obtained gas as a function of some process variables; in particular, the influence of quantity and characteristics of the fed organic material on the process yield was investigated. In Table I the values of the fed fowl manure composition are shown; the reported data are the averages of the measurements taken for five samples (analysis conducted by Cagliari's Chamber of Commerce laboratories) collected in different conditions and localities, albeit in the same geographic area.

The fowl manure was subjected to the slow, wet and catalytic pyrolysis, adding 200 g of water per kilogram of material to this together with catalysts. The gas production was about 0.6 kg per kilogram of fed solid, while its composition and lower calorific value are reported in Table II; in addition to the gas phase, about 0.16 kg of biochar and inorganic components and 0.24 kg of aqueous condensate were produced.

IV. Technical and Economic Evaluation

To demonstrate the sustainability of the proposed process, we report the economic analysis, developed for the realization of a plant to treat two different kinds of vegetable materials; the plant, which will operate with the same pyrolysis process, is designed to serve a town of about 25,000 inhabitants. One of the used materials (kenaf, or *Hibiscus cannabinus L.*) will be obtained from the cultivation of marginal lands, the other one by cleaning the undergrowth (brushwood). The cultivation and use of kenaf have been widely experimented in many areas of Sardinia with extremely positive results [8]. Kenaf plantations will cover an area of about 4,000 ha, while brushwood collection will be carried out in about 5,000 ha. The analysis takes into account not only the realization and management of the the pyrolysis and cogeneration plant, but also chipping operations and transportation to the plant, biomass mixing and the required amounts of added water.

The basic data assumed to determine profitability are reported in Table III, while Table IV shows the data used to calculate costs and revenues of the pyrolysis plant. The design assumptions and considered data allow the economic analysis of the activities for the energetic valorization of the agricultural and forest biomass to be obtained.

The plant, with a power of little more than 20 MW, will be able to count on a constant biomass feed to the pyrolysis reactors of about 13.1 t/h, and on running for 24 hours a day and 330 days a year, considering an annual 30 day stoppage for maintenance. The "dry" agricultural and forestal biomass fed to the pyrolysis reactors is characterized by a medium humidity of 20%; an amount of water is added to this to complete the conversion reactions of the formed coal, with a further formation of hydrogen and carbon monoxide. A plant operating for 330 days a year will reach an electric energy production of about 161,665,000 kWh/y.

TABLE I
ANALYSIS OF THE USED DRY FOWL MANURE

LHV	10,900 kJ/kg
Component	**Weight percent**
carbon	55.68
hydrogen	7.42
nitrogen	8.32
oxygen	4.61
sulphur	0.28
chlorine	0.21
inorganics	23.48

Mean values of five samples.

TABLE II
ANALYSIS OF THE PRODUCED PYROLYSIS GAS

LHV	17,100 kJ/kg
Component	**Volume percent**
hydrogen	58.6
carbon monoxide	16.9
carbon dioxide	15.2
methane	2.6
ethane	0.7
propane	2.0
nitrogen	3.6
others	0.4

TABLE III
ASSUMED DATA FOR THE ECONOMIC ANALYSIS

medium unit production of brushwood	3 t/(ha·y)
medium yield of kenaf chips	25 t/ha
purchase price of brushwood	80 €/t
purchase price of kenaf chips	110 €/t
days of plant operation	330 d
value of Green Certificates (2011)	0.113 €/kWh
value of electric energy (2011)	0.0916 €/kWh
multiplicative factor for short chain (2011)	1.8
duration of Green Certificates	15 y

TABLE IV
ECONOMIC ANALYSIS

Revenues	
Sale of Green Certificates	32,824,400
Sale of electric energy	13,332,000
total revenues	46,156,400
Costs	
staff	1,615,000
Purchase of brushwood	1,350,000
Purchase of kenaf chips	11,000,000
maintenance	3,200,000
Various costs	1,066,700
Fuels/Chemicals	3,705,000
depreciation	7,000,000
Financial charges	2,903,700
total costs	31,840,400
EBITDA	14,316,000

Annual data, in Euros

The EBITDA (earnings before interest, taxes, depreciation and amortization) is equal to about 24,219,700 €/y; considering that the investment amounts to about 70,000,000 Euros, this allows a payback time of slightly less than three years, while the duration of benefits related to Green Certificates and electricity sales in the dedicated market is 15 years.

Finally it should be pointed out that the same authors discussed in a previous work [9] the economic feasibility of the slow, wet and catalytic pyrolysis compared to other biomass to energy processes presented in the literature, concluding that the proposed process presents very promising peculiarities and advantages.

V. Results and Conclusions

The proposed process is capable of treating large quantities of organic matrix materials with a very modest impact on the environment. The extremely positive economic framework (in the case of the proposed example the return time is less than three years) and the modularity of the system allows it to be proposed to both small producers of organic waste (dairies and other small production companies) and structures of a considerable size (local authorities, for the disposal of municipal waste), as well as for the production of energy from dedicated crops (for example, carried out on marginal land). The cost of the produced energy naturally depends on the size of the intervention, but is still modest (on an industrial scale it is in the order of 8-14 €cent/kWh); furthermore, the process is eligible for environmental certification (Green Certificates) for the treating of materials of vegetable origin, with all the resulting benefits in both economic and environmental terms.

The analyses reported in Table II contain two elements that should definitely be highlighted, and that will require further investigation in the subsequent development of a mathematical model of the process: we refer to the high content of CO_2 and C_3H_8 in the produced gas. We believe that the high concentration of CO_2 is due to the high content of oxygen in the organic matrix while instead, the high amount of propane is not due to gas-solid reactions, but to reactions that take place in homogeneous phase in the gas; in fact, while the former present a superficial evolution, and therefore have a modest space in which to occur (probably only the external surface of the particles), the latter have a considerably greater space available and cover three molecular species, two of which (H_2 and CO) are strongly present in the reaction environment.

In addition to these two aspects, the high content of H_2 in the produced gas should be emphasized as well as its complete combustion without the production of lampblack, as found in the performed tests. The fact that the combustion of the pyrolytic gas is possible in the absence of production of unburned and fine dust shows the remarkable potential of the proposed process from the environmental point of view.

The proposed technology has the following advantages:

1. the process can be applied both to agricultural and/or forestry biomass and to waste of any kind provided it contains a carbonaceous matrix (plastic, paper, textiles, putrescible organic matter, etc..);
2. the conversion of biomass to gas is high and the produced pyrolytic gas is so rich in hydrogen that a recovery process of this gas is conceivable;
3. the production of char is minimum while the inorganic components present in the starting material (for example metals of electronic materials) are found in the output as they are, since the process is strongly reducing;
4. the absence of liquid fuel production;
5. the energy requirements of the plant are ensured by the produced pyrolysis gas (on an industrial scale, a consumption equal to about 40% of the produced gas is foreseen);
6. the characteristics of the pyrolysis gas are a guarantee for the quality of emissions, in fact the off-gas of the co-generators used for the production of electrical and thermal energy is extremely clean;
7. plant operation, if used for obtaining energy from wastes, produces one fifth of the emissions of a traditional incinerator at the same feed flow rate; the investment cost of a pyrolysis plant is also much lower than that of an incinerator; another advantage is the recovery of metals in a non-oxidized form, facilitating their valorization;
8. the biochar produced by the pyrolysis of a biomass such as fowl manure is an element of prestige, in fact it contains all the mineral salts useful in agriculture [10].

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