

Optimization of Catalytic Upgrading of Pyrolysis Products

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Biofuel production is an attractive alternative to conventional fossil fuel, effectively solving problems like resource depletion and greenhouse gas emission. Use of solid feedstock and organic wastes to produce biofuel is seen as a promising route from the economical and sustainability point of view. Pyrolysis is one of the possible thermochemical methods to convert solid biomasses to valuable liquid and gas products. However, the bio-oil obtained from pyrolysis can be used as biofuel only after an upgrading step. In fact, raw bio-oil contains various oxygenated organic compounds, which make it unstable, and has high average molecular weight, high viscosity, and low heating value. A suitable method for upgrading bio-oil is catalytic cracking of the pyrolysis products. Catalytic upgrading converts high molecular weight compounds of the bio-oil into lower-weight molecules.

This work investigated the slow pyrolysis and in-situ catalytic cracking of chicken manure in a lab-scale fixed bed reactor. The application to chicken manure is of utmost practical interest, since the pyrolysis process would provide an environmentally safe manner for solving the current problems about disposal of this waste. The catalyst considered was pellet-extruded zeolites (zsm-5). In order to study the effect of influential factors (temperature and catalyst to biomass ratio) on the obtained products, experimental design techniques were used. The process was investigated in both the absence and presence of the in-situ catalyst. The results were statistically analyzed and the influential factors were optimized with the aim of obtaining products with higher quality and heating value. The results can give a clue on how to compromise between the quality of the two potentially valuable products of pyrolysis process (bio-oil and biogas) and the energy requirement of the process.

1. Introduction

Biofuel is a generic term referred to fuel in any form and state that are originated from renewable feedstock (Demirbas 2011). Use of biofuel reduces the dependency on petroleum, and also emission of air pollutant and greenhouse gases (Demirbas 2011). Nowadays, several technologies are available for utilization of biomass both for power generation, and for transportation and production of chemical feedstocks (Kwon et al. 2012). Among them, pyrolysis is a low-cost and promising thermochemical conversion process for biomass energy utilization (Basile et al. 2014), which produces bio-oil, biogas and char (Yang et al. 2012). In most of the cases, bio-oil is considered the most valuable pyrolysis product, which can be used as a source of either chemicals or fuel (Amutio et al. 2013). However, several adverse characteristics of bio-oil urge the need for upgrading processes: bio-oil is unstable and undergoes repolymerization reactions by aging; acidity, high molecular weight, and high viscosity of bio-oil makes bio-oil unfavorable for most practical application if compared with traditional fuels (Nava et al. 2009); high water content of bio-oil may cause some ignition difficulties (Güngör et al. 2012); the heating value can be significantly lower if compared with fossil fuels. All these negative characteristics are usually associated with the oxygenated compounds present in the bio-oil, such as carboxylic acids, esters, aliphatic and aromatic alcohols, ethers, ketones, and aldehydes (Nava et al. 2009). Therefore, bio-oil upgrading has to be effective in reducing the oxygenated compound content of the bio-oil. Several processes have been proposed for upgrading: hydroxygenation, hydrocracking, catalytic cracking, steam reforming and fermentation, each of which with specific application for a particular final product (Patwardhan 2010). Catalytic cracking is a possible process for upgrading of bio-oil: during the catalytic cracking, high molecular weight organics undergo a number of reactions within the catalyst bed and

crack to light organics and gaseous products (Nguyen et al. 2013). Therefore, when the bio-oil is catalytically cracked, it produces more aqueous bio-oil, in addition to coke and biogas. The result is a upgraded bio-oil with increased fraction of hydrocarbons and decreased fraction of oxygenated compounds which is evidence of carbon removal reactions through decarboxylation and decarbonylation on the acidic sites of the zeolite catalyst (Campanella and Harold 2012). This process can be done in-situ by simply mixing biomass feedstock with catalyst or in the downstream of the process, by bringing the pyrolysis vapor in contact with the catalyst.

Another important product of pyrolysis process is the biogas, which is mostly composed of carbon dioxides, carbon monoxides and methane. This product has applications as biofuel, even in the pyrolysis process itself (Paolucci et al. 2016), and is more valuable when the fraction of compounds with high calorific value increases. Through syngas based route biogas can also be converted to other chemical products (Skoulou and Zabaniotou 2013). Although char is considered as a leftover of the process in most of the studies, as a result of high amount of carbon and ash, it can be used for soil amendment application and, at the same time, carbon sequestration in soil (Sohi et al. 2011).

In current work, biomass slow pyrolysis with or without in situ catalytic (zeolite) cracking are investigated for the yield of valuable products. The biomass used was poultry litter, which is an abundant and critical waste to be disposed. Thermochemical conversion of this biomass can be a much better waste management technique rather than conventional disposal and land filling of manure. (Kim et al. 2009). Several researchers have studied the effect of zeolite catalyst on slow pyrolysis of biomass (Güngör et al., 2012) (Choi and Meier, 2013). However, no work was found on catalytic pyrolysis of poultry litter. During the catalytic cracking in a Fixed Bed Reactor (FBR), temperature and catalyst to biomass ratio can affect the distribution and characteristics of the products. Response Surface Methodology (RSM) was used to design a set of experiment with variation of temperature in the range of 400-800 °C and catalyst to biomass ratio in the range from 0 to 1.25. The results were used for modelling and optimization of the process.

2. Experimental

2.1 Materials

The biomass used was poultry litter supplied by a local company (RES, Ravenna, Italy), in the form of cylinders with average diameter 5.4 mm and average length 12.5 mm. Biomass was dried, prior to experimental runs, in an oven for 4 hours at 105°C. Therefore all the yields are referred to the dry basis. Proximate and ultimate characterisation of biomass are listed in Table 1. It can be seen in the Table that the amount of ash in poultry litter is higher than the other types of biomass (e.g. 2.65% for bamboo (Hernandez-Mena et al. 2014)). Poultry litter also contains high amount of nitrogen as a result of significant presence of proteins. This value is only 0.5% for pine wood (Arregi et al. 2015). This high nitrogen value is in the range of nitrogen amount in algal biomass (e.g. 5.8 wt% on DAF basis was reported for *Lyngbia* by (Maddi et al. 2011)).

The catalyst used is T-4480 1/16" ZSM-5 (MFI) extrudate from Clariant company. Zeolite catalyst was put in a furnace at 550 °C in the presence of air for four hours and was kept in a desiccator before the experiments.

Table 1: Proximate and ultimate analysis of biomass

Proximate analysis (wt%, d.b.)				
Ash	Volatile		Fixed carbon	
25	67		8	
Ultimate analysis (wt%, DAF)				
C	H	N	S	O
45.3	7.8	6.0	1.2	39.7

2.2 Methods

The slow pyrolysis process, was performed in a laboratory-scale fixed bed reactor (FBR). The apparatus is described in Gomez-Mares et al. (2012). The sample holder of the reactor was loaded with the appropriate amount of biomass and catalyst mix and axially moved to the hot zone of the reactor, in order to simulate a slow pyrolysis process. Nitrogen (8.5 NL h⁻¹) was used as purge gas in the reactor. The evolved gas was separated in a series of four cold traps. The bio-oil yield was obtained by weighting the traps before and after the process. Non-condensable gases were transferred by the carrier gas to a FTIR analyser for online gas analysis. Concentration of CO₂, CH₄, and CO were obtained by calibration of the instrument on test mixtures (Baniasadi et al. 2016). Char was defined as the biomass residue in the holder at the end of process. Coke was measured using the method suggested by (Aho et al. 2010), with TGA-Q500 thermogravimetric analyzer

from TA Instruments-Water (USA) using the following thermal program: 10 °C/min from 25 °C to 795 °C with an isothermal at 100 °C for 15 minutes under flow of air at 100 ml/min. Products yields are equal to the ratio between the weight of each obtained product and the initial biomass. Carbon elemental analysis of the products was done, in order to investigate the distribution of carbon among pyrolysis products and check the viability of the FTIR results. Thermo Scientific Flash 2000 series analyser was used for this purpose.

Response surface methodology (RSM) was used as design of experiment technique. For non-catalytic runs, only one influential factor (temperature) was considered, while for catalytic runs two factors were considered (temperature and catalyst/biomass ratio). Temperature was studied in five levels in the range of 400-800 °C, and catalyst/biomass ratio in five levels in the range of 0.25 to 1.25. Three replicates were considered in order to check repeatability of the system. A limitation of the catalytic upgrading of slow pyrolysis process is low yield of bio-oil. Therefore, the yield of bio-oil was considered to be the first response. Another response was considered to augment the energy content of the biogas, which is the fraction of combustible gases (CH₄, and CO₂) in the incondensable gas. Higher combustible fraction in gas leads to higher HHV. In addition, the runs at lower temperatures are more desirable, since they consume lower energy. Therefore, optimization was performed with the aim of maximizing the bio-oil yield and the combustibles fraction in the gas, and, at the same time, minimizing the temperature. Design Expert version 9 free trial software (Stat-ease, 2015) was used for design, modelling and optimisation of the process.

3. Results

3.1 Products yield

The yields of the different products obtained from FBR are shown in Figure 1 for both non-catalytic and catalytic process. The catalytic results reported in this graph are for the constant catalyst/biomass ratio of 0.75 which is the middle level in the range. The effect of temperature on the products yields is same for both process. By increasing the temperature, the yield of bio-oil increases as a result of higher conversion. However, at higher temperature (> 500 °C) the bio-oil yield decreases by further thermal cracking and add to the gas. By comparing the non-catalytic and catalytic yields, it can be seen that, the presence of catalyst causes a little decrease in the char yield. The bio-oil yield decreases by catalyst use, since the catalyst transforms the bio-oil by cracking high molecular weight compounds to lower molecular weight ones. Catalytic cracking therefore increase the yield of non-condensable gases at the expense of the bio-oil. Coke is also formed as a result of the catalytic cracking and deposits on the catalyst surface.

Figure 2 illustrates the fitted surface to bio-oil yield obtained in catalytic process as a function of temperature and catalyst/biomass ratio. It can be seen, that the effect of catalyst on the amount of organic bio-oil yield is much less than the effect of temperature. Up to the ratio of 0.75, the increase of catalyst amount leads to lower yield of bio-oil. At higher catalyst/biomass ratios, the bio-oil seems to increase as the amount of catalyst increases. Below 0.75, the catalyst causes cracking of organic bio-oil to gaseous compound and therefore lower amount of total bio-oil is obtained. The increase in total bio-oil yield (this includes aqueous and organic fraction of the bio-oil) for higher catalyst/biomass ratios was explained as an increase in the formation of the aqueous fraction of the bio-oil, as result of the catalytic cracking reactions. The same trend of bio-oil with catalyst amount was observed in the work of Pan et al. (2010).

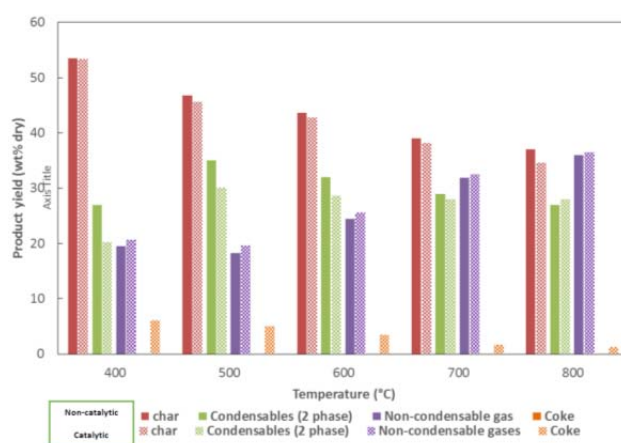


Figure 1: Product yields of non-catalytic and catalytic (catalyst/biomass=0.75) slow pyrolysis of poultry litter

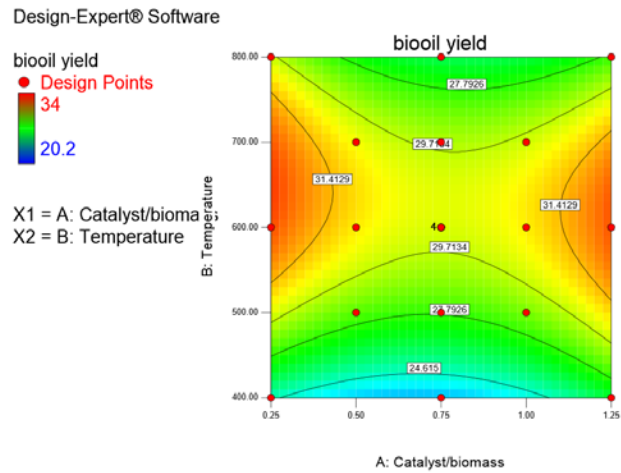


Figure 2: Effect of temperature and catalyst/biomass ratio on the yield of bio-oil

3.2 Combustible fraction of gas

The major components identified by FTIR in the gas were CO₂, CH₄, and CO. Figure 3, shows the obtained concentration curves for the three compounds in a 700 °C test with various catalyst/biomass ratio. It can be seen that by raising the catalyst/biomass ratio, the curves will shift up for all the three compounds. The total yields of the compounds were obtained by integrating the flow rate curves over time.

Figure 4 compares the combustible (carbon monoxide and methane) and non-combustible (carbon dioxide) volumetric fraction of the gas for catalytic (0.75 catalyst/biomass ratio) and non-catalytic tests. For both processes, by raise of temperature, the fraction of combustibles in the gas increases. It can be seen that, at lower temperatures (<600 °C), the gas obtained from catalytic process contains more combustible than the gas obtained from non-catalytic process. At higher temperatures, this fraction is quite the same for both processes.

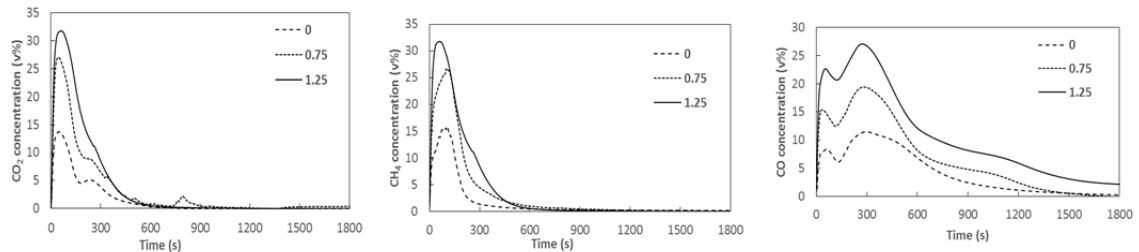


Figure 3: Concentration curve of the gaseous compounds obtained at 700 °C with various catalyst/biomass ratio

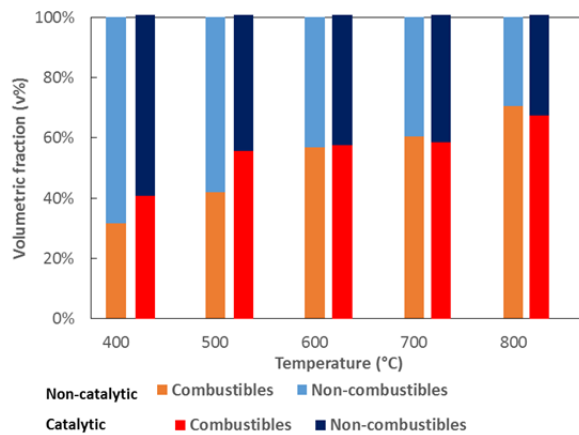


Figure 4: Fraction of combustible compounds in gas for non-catalytic and catalytic (catalyst/biomass=0.75)

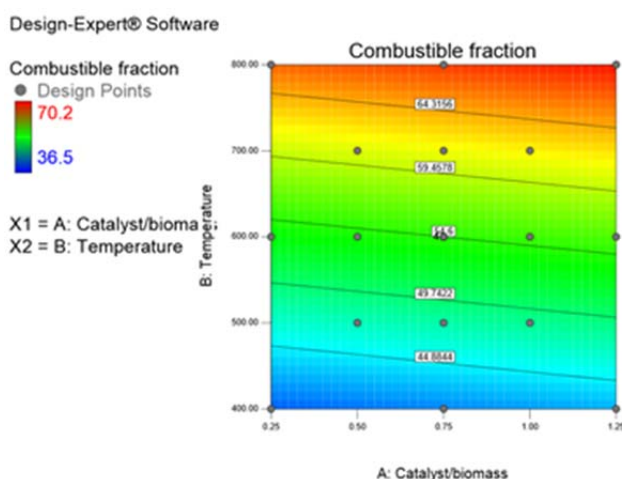


Figure 5: The effect of temperature and catalyst/biomass ratio on combustible fraction of biogas

Figure 5, shows the effect of temperature and catalyst amount on the combustible fraction of biogas. Temperature influences significantly the results, while by raising the catalyst amount, combustible fraction of gas slightly improves.

3.4 Optimization

The optimization was done pursuing three goals: i) maximizing the amount of bio-oil obtained from the process, ii) maximizing the combustible fraction of the biogas, iii) minimizing the energy consumption of the overall pyrolysis process. Therefore, the desirability of each separate operative condition (temperature and catalyst/biomass ratio) was calculated for the three goals above. In defining desirability, the same weight was assigned to all the three goals. Table 2 shows the optimal condition and the expecting responses for non-catalytic and catalytic process. It can be seen that, the optimum temperature for the both processes is in the range of 540- 580 °C. The optimum results was obtained at the maximum amount of catalyst/biomass in the range (1.25).

Table 2: Optimal condition and expecting responses

	Non-catalytic process	Catalytic process
Optimal parameter		
Temperature (°C)	545	577
Catalyst/biomass	n/a	1.25
Results		
Bio-oil yield (wt%)	32.6	35.6
Combustible fraction in gas (v%)	52	54
Desirability score	0.675	0.643

4. Conclusions

This work focused on a preliminary optimization of non-catalytic and catalytic slow pyrolysis of poultry litter. The yield of products were experimentally obtained and the analytical methods were used to characterise the non-condensable products. The results were used to investigate the energy application of the products. It was observed that by use of catalyst, the yield of biogas increases at the expense of bio-oil. Some fraction of bio-oil was cracked also to coke. The on-line analysis of the gas products shows an improved yield of CO₂, CH₄, and CO by catalyst application, and, in particular, the gas obtained from catalytic process contains higher fraction of combustible gases if compared to non-catalytic processes. Both catalytic and non-catalytic processes were optimized with RSM in order to strike a compromise between the energy recovered in products and the heat consumption of the system. Working at the optimum conditions, the bio-oil yield of non-catalytic and catalytic process were 32.6 wt% and 35.6 wt% respectively. The fraction of combustibles in the gas was 52 v% for non-catalytic process, while it was 54 v% for catalytic process. While future work is required for investigating further technical problems (separation of the catalyst, removal of the coke, etc.), this

preliminary study suggests a potential advantages in the catalytic process, in terms of better quality of the gas phase from poultry litter pyrolysis.

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