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Low temperature conversion (LTC) – An alternative method to treat sludge generated in an industrial wastewater treatment station – Batch and continuous process comparison

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ABSTRACT

In this work low temperature conversion (LTC) process was applied in a dried sludge from a petrochemical industry wastewater treatment station located in Rio de Janeiro, Brazil. The process was performed in two modes: continuous and batch-scale. This process produced a pyrolysis oil (continuous 14%; batch-scale 40% yield); pyrolytic char (continuous 46%; batch-scale 56% yield); gas and water. Pyrolysis oil fraction was analyzed by gas chromatographic mass spectrometry (GCMS) and the main components identified were toluene, ethylbenzene, styrene, isopropyl benzene, alpha-methylstyrene, butanenitrile and 1,3- biphenyl propane. Metals content, sulfur content and calorific value have been determined for the pyrolysis oil fraction. The results showed that the pyrolysis oil obtained could be used for industrial purposes and/or as energetic matrix.

1. Introduction

1.1. Pyrolysis – low temperature conversion (LTC)

There are two types of pyrolysis process, conventional (slow pyrolysis) and fast pyrolysis (Mohan et al., 2006; Huber et al., 2006). The terms "slow pyrolysis" and "fast pyrolysis" (Bridgwater, 1995; Bridgwater et al., 1995, 2001) are a function of the time, heating, temperature and products that we desire to get. With these variable of process the types of pyrolysis had been subdivided in: carbonization; conventional; fast; flash – liquid; flash – gas; ultra; vacuum; hydro – pyrolysis and methano – pyrolysis.

The low temperature conversion (LTC) process was initially developed in the 80s by the researchers Bayer and Kutubuddin (Bayer and Kutubuddin, 1999). This process involves pyrolysis around 400 °C and generates liquid products rather than gaseous ones, normally obtained by high temperature pyrolysis. The aim of this process is to produce pyrolysis oil with high caloric value (Bayer and Kutubuddin, 1999). Depending on the sludge origin, the components of pyrolysis oil can be hydrocarbons, fatty acids and aromatic substances in different proportions. The advantage of this process is that pyrolysis oil fraction obtained can be stored and transported. In the case of sludge treatment generated in the wastewater treatment station of the petrochemical industry, it should be possible to feed back oil fraction into the refining process (Bridle et al., 1999, 2002; Bridle and Skrypski-Mantele, 2000; Bridle and Unkovich, 2002). The pyrolytic char obtained can be activated by subsequent partial gasification at a temperature around 900–1500 °C. These fractions may be utilized as filter or as a solid fuel without activation. However, the maximum commercial value is considered to be attained by partial gasification to yield activated carbon. The recovery of activated carbon from wastes has not been commercially investigated yet, but it is increasing attractive since it solves two problems simultaneously: waste disposal and the increasing demand for low-cost adsorbents.

1.2. The sludge – an environmental problem

The sludge residue generated by a petrochemical wastewater treatment station is generally disposed at landfill sites or incinerated. The incinerators used are aggregates of fluidized bed furnaces or rack-type furnaces with a combustion temperature of 800–900 °C. This process results in a residue consisting of dust and ashes, similar to that obtained for incinerated municipal sewage sludge, and which requires to be landfilled. Considering recycling aspects, these methods are unsatisfactory and, in the last few years, several industries and research groups have developed alternative technologies to treat and disposal the sludge.

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The wastewater treatment station of a petrochemical industry receives organic material from the industrial production of nitrilic rubber, styrene-butadiene rubber (SBR) and polybutadiene liquid hydroxylate (PBLH). The wastewater treatment station produces 3600 t/year of sludge that is disposed in a co-processing industry, with a cost of about U$ 15,000,00/year. Low temperature conversion (LTC), which is a pyrolitic process used as an alternative technology in the reuse of a variety of solid waste materials, has been applied on a laboratory scale to treat the sludge using batch and continuous process producing pyrolysis oil, pyrolytic char, water and gas phases (Romeiro et al., 1999, 2000a,b).

2. Objective

This work aims to apply the LTC process to the sludge generated by a wastewater treatment station of a petrochemical industry, using batch and continuous modes in laboratory scale experiments. The process has been studied as an alternative technology for the re-utilization of industrial waste solid materials. Fractions yields and chemical composition of pyrolysis oil, obtained by batch and continuous mode process, have been determined.

3. Methods

3.1. Thermal conversion process of dried sludge in a batch and continuous mode

Sludge samples were dried at 75 °C in an oven for 24 h until constant weight, and processed in the LTC reactor using batch and continuous mode, both of which operated at temperatures around 380 °C. In the batch mode, nitrogen atmosphere (N_2) was used during 3 h of residence time. In the continuous process, the gas from conversion was used and the residence time was about 15 min, with the sample been continuously added into the reactor. The characteristics of the continuous and batch-scale reactors are listed in Table 1.

In the batch-scale, the gas produced is conducted and condensed at temperatures around 15 °C into a separator funnel. The non-condensed gas phase is passed into a trap containing sodium hydroxide solution (10% w/v). Pyrolysis oil and aqueous phases are separated. In the continuous process, the pump gas recycles the non-condensed gas phase.

3.2. Analytical methods

Dried sludge samples were added to the batch and continuous reactor as described. The pyrolysis oil generated during the LTC process of petrochemical sludge at 380 °C was analyzed by gas chromatography mass spectrometry (GCMS). The GCMS analysis were carried out on a HP 6890 Gas Chromatograph instrument connected to a HP 5973 selective mass detector using a HP-5MS column (30 m × 250 μm × 0.25 μm) started at 40 °C held for 7 min with a heating rate of 4 °C/min up to 90 °C held for 5 min, followed by 20 °C/min to 280 °C held for 10 min; injection: 1 μl; split 50:1 and carrier gas helium at 1.5 ml/min. The Hydrogen Nuclear Magnetic Resonance data (1H NMR; tetramethylsilane as standard) were obtained using a Varian-Unity Plus 300 spectrometer. The FTIR spectra were measured on a Perkin Elmer 1420 and Magna – 560 Nicolet (calibrated using polystirene). The relative density analyses were measured using a glass pycnometer Bingham by ASTM – D 941 method. The elemental analysis was determinate according to the ASTM 5291-92 (standard test method for instrumental determination of carbon, hydrogen and nitrogen) using on Perkin Elmer 2400 elementary analyst model. The metals content were measured on a X-ray Philips – PW 1480 spectrometer model equipped with rhodium tube. The calorific value was determined according to ASTM 3286-6 using a Parr calorimeter. The sulfur content was measured using a Leco – SC 432 Model by the ASTM – D 1552-90 method.

4. Results and discussion

In this work a comparison between the two processes was made, batch and continues, in order to compare the experimental, chemical and physical chemistries parameters of the gotten products. The experiments had been made with five repetitions ($n = 5$) and the average relative concentrations of the conversions products are shown in Table 2.

The yields of the individual fractions depend on the LTC mode process used having as main difference the time of retention in the gaseous phase. The continuous process produces higher gas yields compared to the batch process. In the batch process, more than one-third of the weight of the dried matter processed could be recovered as pyrolysis oil. In the continuous process the time of retention of the material in gaseous phase is small, what probably it is responsible for the low pyrolysis oil yield and consequently more char in the end of the process.

The GCMS analyses were carried out on five pyrolysis oil fractions, obtained by batch and continuous LTC processes, (Table 3). Proportions of styrene and alpha-methyl styrene are greater, while that of isopropyl benzene is less. The relative concentrations of toluene and ethylbenzene in the batch process are greater than obtained in the continuous process.

Table 1
The characteristics of continuous and batch-scale reactors

Characteristics of the reactors	Continuous	Batch-scale
Type of oven	Rotators	Fix
Length	15 m	1.0 m
Inside diameter	0.30 m	0.15 m
Working temperature	380 °C	380 °C
Sample mode addition	50 kg/h	700 g
Collector of char	In the end of the reactor	In the middle of the reactor
Vacuum pump	Yes	No
Type of heating	Electricity	Electricity

Table 2
Yields of LTC products by bath and continuous mode

	% Oil	% Char	% Gas	% Water
Bath-scale	40	47	8	5
Continuous	17	63	16	4

Table 3
The chemical composition of principal compounds identified by GCMS analysis in the pyrolysis oil obtained by batch and continuous process at 380 °C

Compounds	RT (min)	RC%	
		Continuous process	Batch process
Toluene	3.39	4.7	7.9
Ethyl benzene	6.54	6.5	11.8
Styrene	8.05	35.8	14.2
Isopropyl benzene	9.85	2.4	4.7
Alpha-methylstyrene	12.72	21.9	8.3
Butanenitrile	27.14	9.2	9.6
1,3-Biphenyl propane	30.14	7.0	7.3

RT – retention time; RC – relative concentration.

However, the relative concentrations of butanenitrile and 1,3-biphenylpropane are similar in both processes. These results indicates that in the continuous process, as the sludge sample is moved into the oven, styrene, that is initially aggregated in the sludge petrochemical sample, is volatized more efficiently than in the batch process. Styrene and alpha-methyl styrene are obtained at higher concentrations in the pyrolysis oil in the continuous mode process. We suggest that in the continuous process, styrene vaporizes and alpha-methyl styrene is formed in the gas phase by a radical reaction, as residence time is smaller compared to the batch mode. The reactions in the gas phase in the batch process occur with less intensity, there is insufficient time to form substances other than ethyl benzene, toluene and isopropyl benzene in relatively high concentrations. On the other hand, in the batch mode, the residence time is greater, substances such as ethyl benzene, toluene and isopropyl benzene can be formed with more facility in the gas phase.

The mass spectra of styrene, isopropyl benzene and alpha-methyl styrene were as expected. The tropylium ion (m/z 91) can be observed in the spectra of aromatic compounds. In the mass spectra of styrene, the molecular and the base peaks were coincident, m/z 104. In the mass spectra of isopropyl benzene, a strong peak at m/z 105 corresponds to the loss of a methyl group with the formation of a methyl-substituted tropylium ion. The molecular ion observed in the mass spectra of styrene, isopropyl benzene and alpha-methyl styrene are respectively m/z 104, m/z 120 and m/z 118 and they are usually intense, in accordance with the literature.

The ^{1}H NMR spectra, of five pyrolysis oil, obtained in the batch and continuous modes, shows δ in the following regions: 7.0–7.8 ppm (aromatic – 30.0% for batch process and 30.0% for continuous process); 5.0–6.8 ppm (olefinic – 5.0% for batch process and 6.0% for continuous process) and 0.8–3.0 ppm (alkyl – 65.0% for batch process and 64.0% for continuous process).

The absorptions observed in the FTIR spectra are in agreement with GCMS data: 3061, 3026, 2926–2857 cm^{-1} (C–H stretching vibrations); 2248 cm^{-1} (C≡N of stretching vibrations of nitriles); 1950–1800 cm^{-1} (overtone bands – aromatic rings); 1602 cm^{-1} (C–H stretching vibrations); 1494 cm^{-1} (aromatic ring vibrations); 1452, 1376 cm^{-1} (methyl absorption); 1030, 907 cm^{-1} (substituted aromatic ring); 776, 698 cm^{-1} (meta – disubstitute aromatic ring).

The elemental analysis and metals concentrations (%) were determined in five samples of dried sludge and in the pyrolysis oil produced by batch and continuous process. The results are listed in Table 4.

Table 4
Average results ($n = 5$) of sludge elemental analysis – dried sludge and O.L. fractions

Parameter	Dried sludge 75 °C (%)	Pyrolysis oil	
		Batch process (%)	Continuous process (%)
C	n.m	86.1	86.3
H	n.m	9.0	8.7
N	n.m	3.6	3.6
Cd	0.0002	n.d.	n.d
Co	0.0001	n.d.	n.d
Ni	0.0006	0.0001	0.0001
Cr	0.0007	n.d.	n.d
Pb	0.0047	n.d.	n.d
Cu	0.0042	0.0001	0.0002
Ba	n.d.	n.d.	n.d
Zn	0.0059	0.0002	0.0001
Mg	0.56	n.d.	n.d
Ca	1.6	0.0006	0.0008
Al	1.7	n.d.	n.d
Si	2.8	0.01	0.01
Fe	1.2	0.0001	0.0001

n.m. = not measured; n.d. = not detected.

Table 5
Fuel parameters analyzed in the pyrolysis oil obtained by LTC

Parameters	Dried sludge	Pyrolysis oil	
		Batch Mode	Continuous mode
Calorific power MJ/kg	24	40.2	40.3
Relative density 20/4 °C	–	0.96	0.98
S%	–	0.36	0.82

The metal analyses performed in the dried sludge sample and in the pyrolysis oil by LTC, in batch and continuous processes, indicate that Cd, Co, Cr, Pb, are totally transported to the gas phase. Moreover Ni, Cu and Zn have only been partially transported, while Al, Si, Ca and Fe were held in the solid fraction.

Fuel parameters are important in the evaluation of the energetic utility of the pyrolysis oil obtained by the use of LTC process during treatment of petrochemical residues. Such parameters include calorific power, relative density and sulfur contents. Those parameters were analyzed and the average ($n = 5$) results are shown in Table 5.

The calorific powers determined for the pyrolysis oil obtained in the LTC batch and continuous processes are similar to those found for fuel oil derived from petroleum. Furthermore, the sulfur content determined is smaller than that generally obtained in fossil fuels (1% m/m). Thus the use of pyrolysis oil can have environmental benefits since the formation of harmful SO_x would be much reduced.

5. Conclusion

Batch and continuous LTC process produces pyrolysis oil with similar chemical characteristics. However, each process shows differences in the yields of the fractions, as well as the relative amounts of aromatic compounds, identified as styrene, alpha-methyl styrene and isopropyl benzene. The fuel parameters of the pyrolysis oil indicate that this fraction is useful energy source.

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