



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.

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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 US \$15,000,00/year. Low temperature conversion (LTC), which is a pyrolytic 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 (N₂) 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 being 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 was carried out on a HP 6890 Gas Chromatograph instrument connected to a HP 5973 selective mass detector using a HP-5MS

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

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 polystyrene). The relative density analyses were measured using a glass pycnometer Bingham by ASTM – D 941 method. The elemental analysis was determined 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 continuous, 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 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.

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