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Breaking down polystyrene through the application of a two-step thermal degradation and bacterial method to produce usable byproducts

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ABSTRACT

In this work, the objective is to examine a novel approach on the biodegradability of polystyrene is examined. A two-step method for the degradation of polystyrene to chemically useful products has been devised. Initially, polystyrene is liquefied via a thermal degradation procedure predominantly into styrene monomers at low temperatures and left to cool down. Application of microorganisms in a second step targets the breaking of the polymer into smaller organic molecules. Microorganisms tested were *Rhodococcus zopfii* stoecker, *Enterococcus faecalis*, *Pseudomonas putida* and *Salmonella* with the last two being the most effective. A third step is required to treat the organic products accordingly. The suggested method exhibits total conversion of polystyrene. While the method has only been examined on a small scale, its potential advantages for the recycling of polystyrene waste, are minimized energy costs due to low temperatures of thermal treatment used and the extremely fast degradation kinetics observed.

1. Introduction

1.1. Objectives of this work

The aim of this work is to break down polystyrene into valuable organic molecules, by utilizing a combination of thermal treatment and application of specific bacteria. The resulting methodology is described in detail so that it can be a part of a complete solution for handling the global polystyrene crisis. The choice of the enzymatic process was based on the known shortcomings of the previously used methods and the potential for an improved process. In the future, biodegradable alternatives may completely replace polystyrene. Presently, however, these environmentally conscious alternatives are more expensive and provide fewer uses than polystyrene. Moreover, these alternatives do not address the thousands of tons of polystyrene that will continue to exist in current landfills even if all polystyrene production were abruptly halted.

1.2. The dilemma of polystyrene

Polystyrene is a ubiquitous product due to its low cost, simple manufacturing, acceptable mechanical properties, and ease of use. Due to its chemical stability, it adds to the phenomenon known as 'white pollution' (Botelho et al., 2004), which is the accumulation of plastics on earth. In India 15,340 tons of white pollution were generated daily during 2013 (Central Pollution Control Board (CPCB) New Delhi, India, 2013). One of the greatest problems humanity faces is the recycling of plastics, with an emphasis on polystyrene (Istadi et al., 2010). The increasing use of plastics has contributed to the depletion of landfill (Chauhan et al., 2008; Blazso, 1997; Karaduman et al., 2001). In fact, polystyrene alone fills up ⅓ of the world's landfills. Burning of plastics is regionally prohibited since it causes great environmental pollution (Kronholm et al., 2006; Liu et al., 2000). It is because of this that polystyrene degradation has attracted so much research interest especially in the last two decades (for example: Yang et al., 2015; Mohee and Mudhoo, 2012).

1.3. Previous attempts and methods of degradation

Polystyrene is considered to be essentially non-biodegradable in the environment (Shah et al., 2008). Biodegradation can be termed as the ability of at least one microorganism to use a synthetic polymer as a sole source of carbon. However, some microorganisms have been isolated that can use synthetic polymers as a sole source of carbon. For polystyrene several fungi have been previously demonstrated to be able to degrade this compound. While in general not many microorganisms are able to degrade synthetic polymers, the rate of degradation is enhanced in composite mixtures of polystyrene and starch. Thermal or photo-oxidation

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of polystyrene can also be used to facilitate degradation by creating carbonyl groups that can then be consumed by microorganisms. Oxidation can also be facilitated with peroxides and various trace metals.

Chemical catalysis of polystyrene decomposition is the most common method used with conversion rates of 70–90%. In general, polystyrene degradation initiates with the formation of a radical (cationic or anionic form depending on the conditions applied). Catalytic processing results in the formation of benzene and methylindane. In contrast, thermal processing yields styrene and styrene oligomers. At higher temperatures other volatile products are also formed like toluene and ethyl benzene. In a relevant work (Lee et al., 2002), clinoptilolite catalysts use has resulted in selectivity towards aromatics of 99% with styrene being the major product. Photocatalytic degradation of polystyrene is possible using a modified nano-TiO_2 catalyst embedded in the commercial polystyrene (Zan et al., 2006). Alternative methods include ultrasound and supercritical acetone.

2. Materials and methods

2.1. Methodology of polystyrene liquefaction

The polystyrene utilized was pre-consumer waste polystyrene. Initially, the polystyrene was liquefied in the low temperature range (approximately 240 °C) and the chosen bacteria were applied after the produced liquid cooled down. This methodology ensures that the spreading of the bacteria is more homogeneous and effective when compared to the application on surfaces where bacterial films are first formed and the enzymatic process progresses under the film. Also, the application of the microorganisms actually acts on the created oil, which now comprises smaller molecular weight fragments.

In our experiment, thermal degradation took place with the use of a Bunsen burner, fume hood and a test tube containing polystyrene samples. To insure uniform heating and minimal thermal gradients, the polystyrene was heated in small samples (20 g at a time) and was constantly agitated during the heating process. The application of the bacteria was followed by 36 h of reaction time, and then the bacterial reactions were terminated by freezing the samples. Equipment used for the bacteria handling comprised of an incubator to grow the bacteria, a consistent environment (of 30 °C) which was optimal for the bacteria to metabolically break down the polystyrene (Loffhagen et al., 2004), a fully equipped microscope to view the physical characteristics of the bacteria once the bacteria was cultured, and a soy-based broth for the bacteria.

2.2. Bacterial strains

The following bacteria were used: *Rhodococcus zopfii* stoecker, *Enterococcus faecalis*, *Pseudomonas putida* and *Salmonella*. Bacteria were grown at 30 °C in a soy-based broth.

2.3. Treatment of polystyrene oil with bacteria

After the oil was cooled, it was added to freshly prepared cultures of bacteria at a 1:10 ratio. The bacteria were then further incubated at 30 °C for 36 h after which the process was terminated by freezing the samples. 30 °C has previously been shown to be the optimal temperature for degradation (Loffhagen et al., 2004). In all tests run, each sample was provided with the same amount of polystyrene 0.62 g, which after melting corresponds to 0.5 ml.

2.4. Preparation of sample for GC/MS

Following the reaction the samples were centrifuged such that the oil was separated from the aqueous phase. The oil was then used in GC/MS analysis.

2.5. GC/MS

The GC–MS process included 5 steps. For each test sample, 300 mg of material was transferred to a clean vial equipped with a septum and allowed to equilibrate for two hours. A SPME fiber was presented to the headspace for 30 min at 60 °C. Immediately after sampling the adsorbed VOCs were desorbed in the GC injector. Desorption time was 3 min at 220 °C. The data were then analyzed using AMDIS software for identification of components in the samples.

For the GC–MS analysis a Waters/Micromass Quattro GC mass spectrometer interfaced to a Thermo Electron Trace gas chromatograph was utilized. A 28 M 0.25 mm ID DB-17MS column was used to separate components. Carrier gas was helium at 1.2 ml/min splitless. For each GC–MS data file, a set of target components was identified with the aid of the AMDIS software. Each of these components was then compared against all compounds comprising the NIST Mass Spectral database. The top hit was reported.

Constant, exact temperatures for the GC column were: injector temperature: 220 °C, initial oven temperature: 80 °C, ramp I 10 °C/min, final temperature I 180 °C, ramp II 15 °C/min, final temperature II 280 °C for 2 min. Several specific MS parameters were the use of ionization and ion polarity EI+, a scan rate 2 scans/s, mass range 45–350 Da, ion source temperature 180 °C, transfer line temperature 250 °C.

The efficiency of the degradation of polystyrene can be mainly attributed to the following factors:

- Enhanced enzymatic action of the bacteria on the monomers, dimers, and oligomer mixture, which was derived from thermal treatment of polystyrene. This enhancement occurs because of the increased mobility of the bacteria in the liquefied polystyrene mixture (vs. solid polystyrene). Other works on enhanced biodegradation activity have shown that such enhancements have been observed for immobilized strains (Hou et al., 2013). Provided that the required population is present, the excess volume: surface ratio caused the bacteria to produce greater degradation rates. In comparison to reported degradation rates from previous studies based on solid polystyrene, the degradation rates reported here are the highest, e.g.: a previous study showed that polymeric degradation in soil after activation required more than 60–90 days for observable change.
- Initial physical in its most common form polystyrene is highly porous (Styrofoam is more than 96% air) thus allowing for microorganisms' insertion and transportation. Even though the initial physical structure is destroyed after thermal degradation, other research groups have discussed the possible microstates of polystyrene. This speculation has been mentioned about polystyrene in foam forms by other research groups as well (Pushpadass et al., 2010).
- The liquid/soft nature of the liquefied polystyrene allowed for huge enhancement of microorganisms activity. A similar effect has been recently reported for diesel oil biodegradation via immobilized microorganisms (Hou et al., 2013). The enhancement in that work was more than 10 times in terms of degradation rates.
- Last, the types of additives and/or plasticizers greatly affect biodegradation rates. As a recent work has shown, different additives led to a 2.3x increase of biodegradation rate of LPDE under microorganism application (Muenmee et al., 2015).

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