



# ATTEMPTS ON PREPARATION OF ELASTIC ABSORBENT FROM WASTE RUBBER TYRES FOR RECOVERY OF BIOBUTANOL FROM FERMENT LIQUORS

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Attempts on the preparation of elastic sorbents from waste rubber tyres, for removal of biobutanol from ferment liquor extracts, using low-distribution apolar solvent like n-heptane have been discussed. The main factors in preparation of useful sorbents are the type of the waste tyre, the type of the sulphonating agent, and the reaction conditions. The waste tyres containing large amount of styrene proved to be useful base material for preparation of elastic sorbent with concentrated sulphuric acid as sulphonation agent. The common mixed waste tyres resulted in elastic sorbents with lower absorbing capacities. Therefore, the styrene containing ones were studied over a wide range of the sulphonation conditions.

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## Introduction

Biobutanol, one of the most promising biofuel of the near-future, is produced in fermentative processes from agricultural products and wastes.<sup>1,2</sup> In order to improve the effectiveness and decreasing the process costs, the so-called extractive fermentation processes are favoured in order to avoid the accumulation of the toxic biobutanol during the fermentation process.<sup>2-4</sup> The most effective extractants like heptanal, however, are toxic, and the non-toxic solvents like aliphatic hydrocarbons such as n-heptane have very low distribution coefficients. Combining the extractive fermentation in the presence of aliphatic hydrocarbon extractants by removing of biobutanol from the low hydrocarbon solvent with a solid phase regenerable super absorbent before recycling that to the fermentation process, is a potential way to solve this problem.<sup>5</sup>

In order to regenerate of the solid sponges with heat treatment (both the absorption and regeneration processes initiate large volume changes of the absorbents due to swelling and drying) in order to prevent the cracking and mechanical destroying, the supersorbents used for recovery of butanol and similar polar solvents should be elastic.

In this communication the preliminary results on attempts on preparing a cheap, elastic and regenerable solid supersorbents for recovery of biobutanol from apolar

aliphatic hydrocarbon extractants used in the extractive biobutanol fermentation processes are described starting from waste rubber tyres.

## Experimentals

### Sulphonation of the soft waste rubber tyres

A waste soft rubber tyre granulate (sample made from a cross motor tyre cubes with putting that into liquid nitrogen and grinding the cooled inelastic form with selecting a fraction with 2.5 mm average equivalent diameter) (4.1 g) was mixed with 4 ml 1,2-dichloroethane and 50 ml of 96 % sulphuric acid at room temperature. The reaction mixture was heated until 90 °C in 2 h then kept at this temperature for 3 h, and cooled left to cool to room temperature (roughly 1.5 h). The sample was thoroughly washed with water until acid-free and the ion-exchange and salt-splitting capacities were measured with a standard method.<sup>6</sup>

The water content was measured with drying the samples in an oven at 105 °C. Solvent absorbing capacities were measured with gravimetrically after keeping the sample in the appropriate solvent for an hour. Both the salt-splitting and the ion-exchange capacity were found to be 0.50 mequiv mL<sup>-1</sup>. The binding capacity for n-BuOH and some other solvents including water is given in Table 1.

### Sulphonation of the hard waste rubber tyres at high temperature

A waste hard rubber tyre granulate (made from a hard tyre cubes with putting that into liquid nitrogen and grinding the cooled inelastic form with selecting a fraction with 2.5 mm average equivalent diameter) (4.4 g) was mixed with 1,2-dichloroethane (4 mL) and 90 g of 96 % sulphuric acid at room temperature. The reaction mixture was heated until 90 °C in 2 h then kept at this temperature for 3 h, and cooled left to cool to room temperature (roughly 1.5 h). The sample was thoroughly washed with water until acid-free. The n-butanol and water absorbing capacities were found to be 21.6 and 147.0 %, respectively. The salt-splitting capacity was found to be 0.31 mequiv mL<sup>-1</sup>.

**Sulphonation of the hard waste rubber tyres at room temperature**

The common waste tyre granulate (30 g) removed from car tyres prepared in a method given previously was swelled with 20 mL of 1,2-dichloroethane for 30 min, the excess of solvent was decanted and the sulphonation was performed with 120 g of 96 % sulphuric acid at room temperature for 3 h. The same methods as previously described were used to isolate and characterize the product. The salt splitting/ion exchange capacity was found to be 0.21 mequiv. mL<sup>-1</sup>.

**Effect of sulphuric acid on the sulphonation of the hard waste rubber tyres at room temperature**

The common waste tyre granulate (25 g) removed from waste tyres prepared in a method given previously was swelled with 47.7 mL of 1,2-dichloroethane for 30 min, the excess of solvent was decanted and the sulphonation was performed with 500 g of 96 % sulphuric acid at room temperature for 3 h. The same method was used to isolate and characterize the product as earlier. The salt splitting/ion exchange capacities were found to be the same, namely 0.09 mequiv mL<sup>-1</sup>.

**Attempts on sulphonation of waste hard rubber tyres with chlorosulphonic acid**

Waste tyre granulates (5 g, 2.5 mm fraction) were swelled in 25 mL of 1,2-dichloroethane for 30 min, the solvent was removed by decantation, then 40 g of chlorosulphonic acid was added at room temperature with stirring. The reaction mixture was heated until 40 °C in 30 min, when a weak gas evolution was started with strong H<sub>2</sub>S smell. The gas evolution was decreased after 1.5 h and the reaction mixture was allowed to cool for 30 min. The product was a strong tar-like substance which could not be removed and processed.

**Attempt on sulphonation of waste rubber tyres with chlorosulphonic acid without outer heating**

Another portion of (20 g) of waste tyre granules (*d* = 2.5 mm) was mixed with 175 g of chlorosulphonic acid, when the reaction mixture was warmed up to 35 °C. After 10 min stirring, the granulates were disintegrated into powder.

**Attempt on sulphonation of waste rubber tyres with chlorosulphonic acid with ice-cooling**

Five gram of waste tyre granules (2.5 mm in average equivalent diameter) were swelled for 15 min in 25 mL of 1,2-dichloroethane, the mixture was cooled to 5 °C with ice and 10 mL of chlorosulphonic acid was added dropwise in an hour. The maximal temperature was observed due to reaction heat at half of the acid adding (~14 °C). The mixture was stirred for 10 min at 5 °C, and the mixture was poured into ice cubes. No further reaction (evolution of HCl gas) was observed with the residual chlorosulphonic acid.

The solvent was removed by distillation, the residue was washed five times of 400 mL of distilled water. The product was inelastic.

**Swelling experiment with  $\alpha$ -methylstyrene**

Common waste rubber tyre granulate (2.5 mm in diameter in average, 7.14 gram) was mixed with 11.95 g of  $\alpha$ -methylstyrene as swelling and copolymerizing agent, and the mixture was polymerized with 0.5 % dibenzoyl peroxide. The polymer product was a sticky material which could not be isolated from the reactor.

**Results and Discussions**

Extractive fermentation with using non-toxic extractants like aliphatic hydrocarbons results only low distribution coefficients. For example, this value is 0.21, 0.056 and 0.16 for n-BuOH, ethanol and acetone (ABE fermentation products) with 0.031 water equilibrium ratio.<sup>7</sup> In order to remove these solvents, especially the most toxic n-butanol, a solid absorbent is needed, which is in contact with the non-toxic extractant<sup>5,8</sup> before recycling that into the extractive fermentation.

There are known some polar solid absorbents which can absorb butanol and the secondary solvents of butanol production as well,<sup>5,8</sup> together with the small amount of water which exists in the n-heptane in contact with the aqueous ferment liquor. The two most promising ones among them are the sulphonated<sup>5</sup> and nitrated<sup>8</sup> styrene-divinylbenzene copolymers. The sulphonated styrene-divinylbenzene copolymers are commercialized as microporous sulphonated cation exchangers.<sup>6</sup>

The main problem is with using these polymers are, that during absorption of the n-BuOH and other solvents a strong swelling and volume increasing can be observed, and during removal of the solvents from the solid sorbents (regeneration and solvent collection with thermal treatment), a strong volume contraction takes place. Alternate volume changes during the repeated use and regeneration cause formation of cracks and mechanical powdering of the solid absorbent granules.

This is a strong disadvantage due to material loss and technological problems caused by the powder formation. Since the sulphonated polymers are more polar and bound less with aliphatic hydrocarbon solvents than the nitrated ones, our efforts were focused on preparation an elastic type sulphonated type polymer material.

From economic point of view, the best choice as elastic polymer materials for sulphonation experiments was different kinds of waste rubber tyres. Two series of waste rubber tyre materials, namely a soft rubber with high styrene content and a hard rubber (average mixture of waste car rubber tyre processing) were used.

**Table 1.** Solvent absorbing capacity of the raw waste tyres granulates and the sulphonated soft rubber tyres\*

| Solvent                            | Raw soft waste tyre      |                    | Dry sulphonated soft tyre |                  | 69.5 % water contg. sulphonated rubber |
|------------------------------------|--------------------------|--------------------|---------------------------|------------------|--|
|                                    | Absorbed amount, g/100 g | Swelling in vol. % | Absorbed amount, g/100 g  | Swelling, vol. % | Absorbed amount, g/100 g               |
| n-Butanol                          | 7                        | 7                  | 63                        | 87               | 27                                     |
| n-BuOH-H <sub>2</sub> O=82:12, v/v | -                        | -                  | 12                        | -                | -                                      |
| Ethanol                            | 5                        | 5                  | 73                        | 102              | -                                      |
| Ethanol:water, 1:1, v/v            | -                        | -                  | 37                        | -                | -                                      |
| Methanol                           | 10                       | 10                 | 75                        | 105              | -                                      |
| Methanol:water, 1:1 (v/v)          | -                        | -                  | 39                        | -                | -                                      |
| 1,2-Dichloroethane                 | 292                      | 200                | 92                        | 87               | 39                                     |
| n-Heptane                          | 24                       | 28                 | 37                        | 60               | 6                                      |
| Water                              | 0                        | -                  | 87                        | 97               | -                                      |

\*Prepared from a soft rubber (removed from a cross-motor) tyre

Since the sulphonation of polystyrene-butadiene rubbers with chlorosulphonic acid was not thermodynamically favourable ( $\Delta H^0$ ,  $\Delta S^0$ , and  $\Delta G^0$  were found to be 40.708 kJ, 64.22 J K<sup>-1</sup>, and 22.916 kJ, respectively),<sup>9</sup> the sulphonation of styrene-based rubbers was tested only with sulphuric acid, while the common waste tyre rubber mixtures were tested with both cc. sulphuric acid and chlorosulphonic acid.

#### Preparation and properties of the high-styrene content sulphonated (soft) waste tyres

Sulphonation of soft waste tyres containing high amount of styrene (2.5 mm equivalent diameter) and swelled in 1,2-dichloroethane with concentrated sulphuric acid at 90 °C led to black coloured granulates having the expected elastic properties. The prepared air-dried sample contained 69.5 % water which was transformed to dry at 105 °C in an oven. The bulk density of the water-containing and the dry samples was 1.1762 g mL<sup>-1</sup> and 0.4761 g mL<sup>-1</sup>, respectively. This shows highly porous structure of the formed resins. The ion-exchange capacity is the same as the salt-splitting capacity, so the all active groups proved to be strongly acidic sulphonic groups in the resin.

The solvent absorbing capacities and the volume changes during swelling in the given solvent are presented in Table 1. The pure butanol absorbing capacity of the dry resin was found to be 63 % with 87 % of volume changes. The resin without drying can absorb 27 % butanol. Taking into consideration the water content of the wet resin, the absorbing capacity of the dry material content in the wet resin is close to the result get in case of the oven-dried sample.

Comparing the absorption of other polar solvents such as ethanol, methanol, 1,2-dichloroethane and water with the dry resin, the absorbing capacities correlate with the polarity of the solvents. The more polar solvent the more solvent can be absorbed, which unambiguously support the assumption that the active sites of sorption are located in the environment of the polar sulphonic groups. The apolar n-heptane was absorbed only in 37 % and 6 % amount in case of dry and wet resin, respectively. The swelling of dry resin was found to be 39 %. It shows that only the pores play role in absorption of heptane.

The distribution coefficient of the water between the ferment liquor and the extractant selected is a key parameter in the design of biobutanol production technology, because

the presence of water decreases the absorption of polar solvents in a large extent. The butanol absorbing capacity decreases to 12 % in the case of 88 % BuOH-12 % H<sub>2</sub>O mixture (v/v), while in case of 1:1 (v/v) mixtures of ethanol or methanol the absorbing capacity roughly decreases to the half of their original values.

The elastic sulphonated rubbers are promising candidates for recovery of the solvent mixtures from n-heptane before recycling that in the extractive ABE (acetone-butanol-ethanol) or IBE (isopropanol-butanol-ethanol) fermentation processes due to two reasons. First, the distribution coefficient values of n-butanol and other polar solvents between n-heptane and water. Secondly, the low solubility of water in n-heptane, butanol and other polar or less polar solvent containing n-heptane mixtures at low polar solvent concentration.

#### Preparation and properties of the sulphonated common (hard) waste tyres

The sulphonation of a rubber mixture (2.5 mm in average diameter) prepared from common waste tyres were studied in detail both with cc. sulphuric acid and chlorosulphonic acid in a wide range of reaction conditions. In the case of chlorosulphonic acid the efforts failed, because tar-like or powdered material formed in every case, even if the reaction was proceeded with strong cooling. If the reaction proceeded with gentle heating, malodorous gas (H<sub>2</sub>S or mercaptans) were formed which strongly suggests that the disulphide bridges decomposes under the action of chlorosulphonic acid which can explain the formation of tar-like products.

Using concentrated sulphuric acid, the ion-exchange/salt-splitting capacities are the same, but these values are lower than in case of styrene-containing soft rubbers. The more drastic conditions (excess of acid, higher temperature) were used, the less sulphonic acid groups were built into the structure, and there were no elastic products formed in any of the cases. The ion-exchange capacity values decreased from 0.31 mequiv mL<sup>-1</sup> to 0.09 mequiv. mL<sup>-1</sup>, which suggest that the sulphuric acid decomposes the sites where the sulphonyl groups could be attached. Similarly, loss of the elastic properties of the starting rubbers shows that the disulphide bridges are also decomposed during the sulphonation process. Since the chemical environment of disulphide bridges in case of styrene containing starting polymer chain might be

different, the favoured reaction was the sulphonation of aromatic ring and not the decomposition of disulphide bridges in the case of soft rubber tyres.

In order to introduce aromatic ring content into the waste common rubber tyres, to mimic the styrene-based rubbers, the swelling of common rubbers was done with  $\alpha$ -methylstyrene before sulphonation. We expected that the aromatic ring containing product will be more advantageous for preparation of products with sulphonated group, keeping the elasticity of the starting rubber. The polymerization was started with 0.5 % dibenzoyl peroxide, however, the polymers formed cannot be removed from the reactor, a tar-like sticky material was only formed, so the sulphonation tests could not be performed. .

Further studies on usage of the sulphonated elastic soft-rubber tyre based resins as biobutanol supersorbents in ABE and IBE extractive fermentation in the presence of aliphatic hydrocarbons as extractants are in progress.

## Conclusions

The styrene-containing waste rubber tyres are valuable raw materials to prepare sulphonated elastic superabsorbent butanol sponges. The sulphonation of rubber tyres was performed with concentrated sulphuric acid, chlorosulphonic acid led to useless tar-like products at various reaction conditions. The common waste tyres resulted products with lower biobutanol absorbing ability and non-elastic properties led to limited applicability in extractive biobutanol fermentations.

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