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## RESEARCH NOTES

Chemically Enhanced Separation of H<sub>2</sub>SO<sub>4</sub>/HI Mixtures from the Bunsen Reaction in the Sulfur–Iodine Thermochemical CycleVincenzo Barbarossa,<sup>\*,†</sup> Giuseppina Vanga,<sup>‡</sup> Maurizio Diamanti,<sup>†</sup> Massimo Calí,<sup>‡</sup> and Giancarlo Doddi<sup>‡</sup>

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The Bunsen reaction identifies the chemical formation of sulfuric acid and hydriodic acid when sulfur dioxide is oxidized by molecular iodine in aqueous solutions. This reaction occurs spontaneously in a temperature range of 293–373 K and is one of the three steps of the sulfur–iodine thermochemical cycle capable of producing hydrogen from water. In order to attain this, the handling of the H<sub>2</sub>SO<sub>4</sub>/HI mixture is crucial for the thermal decompositions which follow. In our study, we propose an innovative way to separate the acids by using an intermediate insoluble sulfonic acid which forms during the process. This procedure results in two main advantages: (1) the common problem of large quantities of iodine in excess is avoided and (2) less water is used.

## Introduction

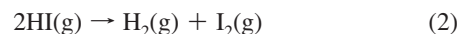
**General Remarks.** The amount of the world’s fossil fuel deposits, including carbon, crude oil, and natural gas, is estimated to be sufficient to cover the world’s energy demands for the next few centuries only. Nevertheless, environmental concerns, combined with the increasing cost of traditional fuels, stress the vital role played by research on alternative and innovative energy sources.

Keeping this in mind, it is generally expected that any timely and future research will take into consideration the greenhouse effect. Consequently, attempts to explore the use of energy sources with no carbon content are particularly welcomed.

One possible answer to the foregoing dilemma is represented by hydrogen with its potential as an effective energy carrier combined with its CO<sub>2</sub>-free production routes. These two advantages are so attractive that worldwide research is currently being undertaken. Understandably, the main carbon-free raw material for hydrogen production is water. Despite its unlimited availability, direct thermal decomposition requires extremely high temperatures that pose serious technological and economic problems. As a consequence, the research has focused on alternative solutions. In this regard, thermochemical cycles are a much better choice in that hydrogen can be extracted from water without the thermodynamic limitation caused by direct dissociation.

Keeping in mind this research approach, the cycles that hold great promise of success belong to the sulfur family.<sup>1</sup> Among them, the so-called sulfur–iodine (SI) cycle has been extensively studied at the bench scale loop level over the past few years.<sup>2,3</sup> This method was originally proposed by General Atomic<sup>4</sup> as a side cycle in nuclear plants in order to receive high temperature waste heat flows; essentially, it can be summarized as follows:

The cycle operates at moderate and high temperatures (298–1200 K) and includes the following three reactions:



The first step (1) is known as the Bunsen reaction, characterized by an exothermic combination of I<sub>2</sub> and SO<sub>2</sub> in aqueous solution. The products are two acids (H<sub>2</sub>SO<sub>4</sub> and HI) that are thereafter thermally decomposed according to reactions 2 and 3. As shown on the right-hand side of these two reactions, the final products, I<sub>2</sub> and SO<sub>2</sub>, can be used to sustain the Bunsen reaction so that the cycle is closed.

Although the sustainability of the reaction chain appears appealing, the usefulness of the SI cycle depends on the critical problems related to the separation and purification of the various chemical components. Most importantly, the purity of reactions 2 and 3, occurring during the gaseous phase, is guaranteed by the efficient separation of the products of the Bunsen reaction.

**Specific Problem Approach.** With this aim in mind, several methods have been proposed to deal with H<sub>2</sub>SO<sub>4</sub>/HI mixtures; these methods are based on the following:

- (i) electrochemical separation;<sup>5</sup>
- (ii) nickel powder addition;<sup>6</sup>
- (iii) use of liquid SO<sub>2</sub>;<sup>7</sup>
- (iv) use of alkyl phosphates or alkyl phosphonates;<sup>8</sup>
- (v) use of precipitation agent and solid salt formation;<sup>9</sup>
- (vi) iodine excess addition.<sup>10</sup>

The most widely used strategy relies on iodine excess addition (method vi) that causes the separation of the aqueous solution into two distinct phases, each one migrating to a well-defined spatial location in the solution. The upper phase contains H<sub>2</sub>SO<sub>4</sub> with little contamination of HI and I<sub>2</sub> (for this reason, it is also known as the sulfuric phase). The lower phase is heavier and contains species of HI<sub>*x*</sub> with *x* > 1 (hydriodic phase). This distinct separation takes place due to the iodine concentration, the increase of which, owing to the induced iodine excess, gives the hydriodic phase higher density, (whereas the sulfuric phase density remains almost unaltered). A good, two-liquid phase

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separation would be when the density of the hydriodic phase is higher than 2.4 g/cm<sup>3</sup>.<sup>11</sup> Our recent study<sup>12</sup> and the work of Sakurai et al.<sup>13</sup> reported the separation characteristics of the two-liquid phases and their dependence on the temperature of reaction and iodine concentration. The iodine concentration is found to be the main parameter that affects the separation process: the higher the I<sub>2</sub> concentration, the better the separation characteristics. But, the effect of the iodine concentrations is not only limited to the phase separation; it also controls the side reactions in the H<sub>2</sub>SO<sub>4</sub>/HI system that are responsible for sulfur and hydrogen sulphide formation. In particular, there is evidence that temperatures below 368 K prevent the occurrence of the side reactions as long as the *x* value in HI<sub>*x*</sub> lies between 4.41 and 11.99.<sup>14</sup> Furthermore, an accurate control of the in- and out-flow at the Bunsen reactor is also required to preserve the two-liquid phase separation. Due to these constraints a narrow optimal operating parameters range has been reported for the Bunsen reaction in the SI cycle.<sup>15</sup>

Iodine excess addition gives rise to some experimental intricacies. For instance, the handling of high I<sub>2</sub> concentrations requires a careful thermometric control in every part of the apparatus, including the pipelines and valves. As a matter of fact, the risk of line plugging due to iodine precipitation must be minimized. Finally, the large excess of water and iodine generate an increase in operating costs for the overall process.

None of these methods satisfies all the requirements for a direct industrial process application, and therefore, it is hoped that alternative solutions are put forward.

The problems mentioned above can be overcome by adopting a new chemical route to obtain the separation of the H<sub>2</sub>SO<sub>4</sub>/HI mixture. As demonstrated recently by some of us,<sup>16</sup> the new method consists of using an aromatic polymer to capture the sulfuric acid so that a sulfonic polymer is created. If an insoluble polymer is used, the sulfonic polymer can be simply separated by filtration. At this point, an acid desulfonation restores the sulfuric acid and the initial aromatic polymer. Various polymers are suitable for the process. In particular, a sulfonation reaction has been reported recently for poly styrene-divinyl-benzene (PSDVB),<sup>17</sup> poly ether(ether)-ketone (PEEK),<sup>18</sup> poly benzimidazole (PBI),<sup>19</sup> and poly phenyl-quinoxaline (PPQ).<sup>20</sup>

In the present paper, we report the preliminary results of our chemical route on PSDVB. The formation of sulfonic-poly styrene-divinyl-benzene (S-PSDVB) and its desulfonation are outlined, and their introduction in the sulfur-iodine thermochemical cycle for hydrogen production is proposed.

## Experimental Section

At first, the sulfonation reaction was carried out in batch conditions. The polymer, PSDVB 300–800 μm beads (Aldrich), was used as supplied. A 2 g portion of polymer was sulfonated by reaction with 44 mL of H<sub>2</sub>SO<sub>4</sub> 96% wt. (Carlo Erba RPE), at room temperature (298 K) and 373 K. The time of reaction was fixed at 4 h, giving a dark brown powder of S-PSDVB that was repeatedly washed with deionized water and vacuum-dried.

The desulfonation reaction was carried out by heating the sulfonated polymers in sealed Pyrex tubes together with 4 mL of sulphuric acid solutions in order to have different pH values (pH = 1, 3, 4). The tubes were inserted in a stainless steel reactor (Parr Instrument), which was partially filled with distilled water; the temperature was maintained at 553 K. The pressure inside the reactor reached 6 MPa, while the reaction time varied between 2 and 6 h.

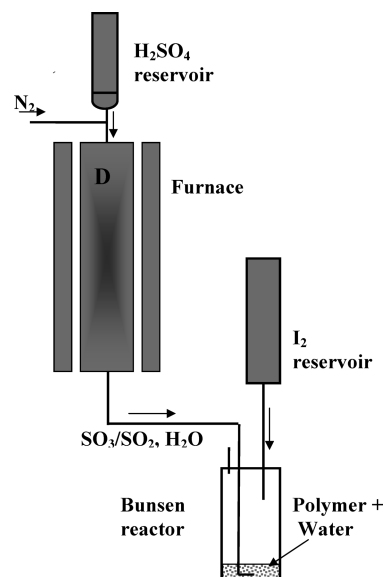


Figure 1. Experimental apparatus for online sulfonation.

The products of sulfonation and desulfonation were analyzed by Fourier transform infrared (FT-IR) spectroscopy (Varian FTS 1000), acid–base titration (Metrohm Titrando 809), and elemental analysis (Carlo Erba EA 1110).

The ion exchange capacity (IEC) was obtained by adding an excess of NaOH 0.1 N to the S-PSDVB, then titrating with HCl 0.1 N and using the following formula:

$$\text{IEC}(\text{equiv/g}) = (\text{equiv NaOH} - \text{equiv HCl})/m_{\text{S-PSDVB}}$$

where  $m_{\text{S-PSDVB}}$  is the amount, in grams, of the sulfonated polymer.

The sulfonation degree (DS) was calculated from the previous IEC value:

$$\text{DS} = \text{IEC} \times \text{MW}_{\text{PSDVB}}/1 - (\text{IEC} \times \text{MW}_{\text{SO}_3})$$

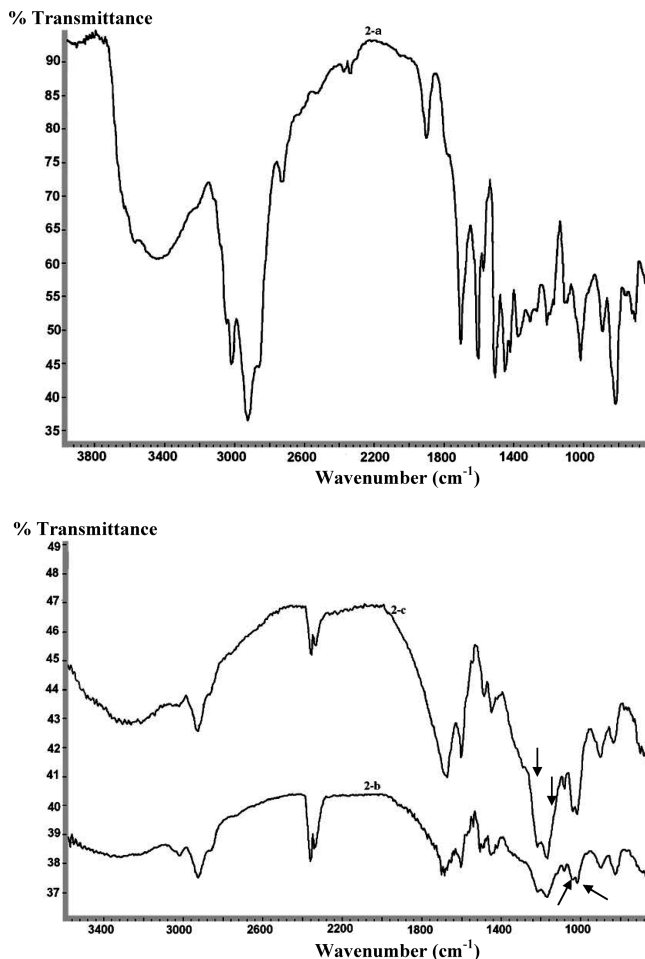
where  $\text{MW}_{\text{PSDVB}}$  and  $\text{MW}_{\text{SO}_3}$  are the molecular weight of the polymer and of the SO<sub>3</sub>, respectively.

The same analytical procedures were applied to analyze the sulfonation reaction taking place in flow conditions in the apparatus shown in the diagram in Figure 1. The sulfuric acid was supplied to the decomposition reactor by a dosing system (Metrohm Dosimat 665). The decomposition reactor was a quartz tube (700 mm length, 36 mm internal diameter) inserted into an electrical furnace (Carbolite TZF model); the furnace temperature during the experiments was 1073 and 1123 K. More detailed information on the sulfuric acid decomposition can be found in a previous paper of the authors.<sup>21</sup> The gaseous products coming from the decomposition reactor and iodine were injected into the Bunsen reactor that contained the PSDVB powder dispersed in a small amount of water. The Bunsen reactor, a Pyrex vessel with jacket, was heated to 353 K.

Sulfur compounds and iodide concentrations were determined using a Metrohm 761 compact ionic chromatograph, with an anion column (Metrosep A SUP 4). The eluant solution was 1.8 mM in Na<sub>2</sub>CO<sub>3</sub> and 1.7 mM in NaHCO<sub>3</sub>.

## Results and Discussion

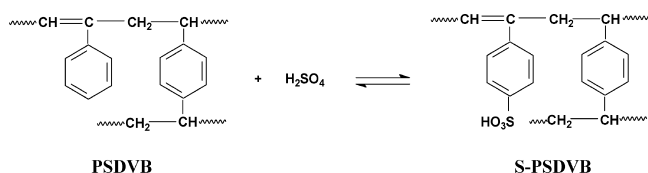
The sulfonation reaction on aromatic molecules is a well-known reaction that has been extensively used since its discovery



**Figure 2.** IR spectra for (a) PSDVB; (b) S-PSDVB at room temperature; (c) S-PSDVB at 373 K.

in the mid of 19th century.<sup>22,23</sup> Consequently, we will not discuss the reaction here. Our focus, instead, is on its application to PSDVB.

The first step necessary to verify the occurrence of the sulfonation reaction on PSDVB was taken in batch conditions (see the Experimental Section) according to the following scheme:



It is helpful to compare the weights of PSDVB and S-PSDVB for experiments running at two different temperatures (room temperature and 373 K) with a reaction time of 4 h. The starting weights of PSDVB were 2.064 and 1.571 g for room temperature and 373 K, respectively. After sulfonation, the weights of S-PSDVB were 2.227 and 1.967 g for room temperature and 373 K, respectively.

The effect of the temperature on the sulfonation is clearly indicated by the increase of the weight as a function of this parameter (7.9% at room temperature, 25.2% at 373 K).

FT-IR reflectance spectra are shown in Figure 2a for PSDVB and Figure 2b and c for S-PSDVB, obtained at room temperature and 373 K, respectively. The spectra 2b and c show the presence of C—S and S=O stretching signals at 1231, 1193, 1115, and

**Table 1.** Elemental Analysis, Ion Exchange Capacity, and Sulfonation Degree for PSDVB and Sulfonated Samples

sample	content (wt %)			IEC (mequiv/g)	DS %
	S	C	H		
A <sup>a</sup>	4.6	58	6.2	1.75	47.8
B <sup>b</sup>	6.8	52.2	5.85	2.4	69.7
C <sup>c</sup>		85.3	7.2		
D <sup>d</sup>	11.2	34.8	6	2.6	77

<sup>a</sup> S-PSDVB prepared at room temperature. <sup>b</sup> S-PSDVB prepared at 373 K. <sup>c</sup> PSDVB. <sup>d</sup> Reference material (Dowex).

1053 cm<sup>-1</sup>. It is clearly evident that the stretching bands around 1200 and 1000 cm<sup>-1</sup> are relatively more intense in the 2c spectrum than in the 2b spectrum. Moreover, the results of the elemental analysis are in accord with the above observations. Table 1 reports the values obtained for the S-PSDVB samples prepared at room temperature (sample A) and at 373 K (sample B). Samples C and D refer to the PSDVB raw material and to a reference material (Dowex AG50W-X8), respectively. The values of the ion exchange capacity (IEC) and the sulfonation degree (DS) parameters are also reported in Table 1. These data suggest that at 373 K there is an increase in both the sulfur content and the degree of sulfonation.

The feasibility of online sulfonation was verified by conveying the H<sub>2</sub>SO<sub>4</sub>/SO<sub>3</sub>/SO<sub>2</sub> mixture from the sulfuric acid decomposer to the Bunsen reactor.

The experimental apparatus is shown in Figure 1. The liquid sulphuric acid was supplied to the thermal decomposer (D) by a dosing pump using an N<sub>2</sub> flux as a carrier gas. The H<sub>2</sub>SO<sub>4</sub> feed flow was 0.3 mL/min, and the N<sub>2</sub> flow was 500 sccm. The gaseous flux from the thermal decomposition reactor is composed of N<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, SO<sub>3</sub>, SO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O. The composition of this mixture is a function of the furnace temperature and is affected by a possible catalyst. Three different furnace temperatures were set: 923, 1023 and 1073 K. The Bunsen reactor was maintained at 353 K. The sulfonation mixture, SO<sub>3</sub> (20%–80%) and SO<sub>2</sub> (80%–20%), is dependent on the decomposition temperature.<sup>21</sup>

Due to experimental difficulties, we were unable to carry out a weight measurement. On the other hand, the occurrence of sulfonation was checked by elemental analysis, acid–base titration, and IR spectroscopy. The sulfur content of the product of the online sulfonation of 2.08 g of raw PSDVB in 40 mL of water, with the furnace temperature set at 1073 K, was 3.43%; the IEC and DS were 0.84 mequiv/g and ~20%, respectively. The low grade of sulfonation is also confirmed by the weak intensities of the sulfonic group bands reported in the IR spectrum (Figure 3). The dilution of the reagent mixture in the Bunsen reactor may account for this result.

To increase the degree of sulfonation, the water content in the Bunsen reactor was reduced to slightly more than the stoichiometric amount and the iodine was added step by step according to its extinction rate. In this way, we were able to obtain a higher sulfonation degree. This is confirmed in Table 2, where the elemental analysis of three samples obtained at different furnace temperatures are reported: sample A at 923 K; sample B at 1023 K; and sample C at 1073 K; sample D is the reference Dowex polymer (as in Table 1). Clearly, the increase of the furnace temperature is responsible for the increase of the sulfur content, thus suggesting greater sulfonation. Since the decomposition of the sulfuric acid at higher temperatures produces more SO<sub>2</sub> with respect to SO<sub>3</sub>, the previous results underline a key role of SO<sub>2</sub> played in the sulfonation mechanism occurring in the Bunsen solution.



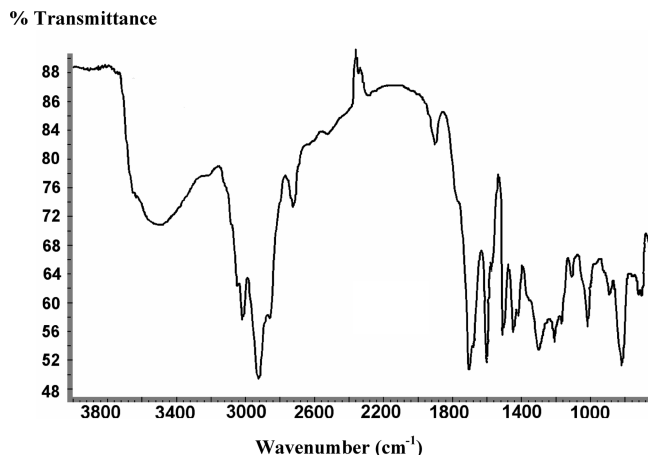


Figure 3. IR spectra for sample from online sulfonation.

Table 2. Elemental Analysis for Online Sulfonation

sample	content (wt %)		
	S	C	H
A <sup>a</sup>	0	77.1	6.6
B <sup>b</sup>	2.7	73.6	5.7
C <sup>c</sup>	9.7	70.9	5.9
D <sup>d</sup>	11.2	34.8	6

<sup>a</sup> Furnace temperature 923 K. <sup>b</sup> Furnace temperature 1023 K.

<sup>c</sup> Furnace temperature 1073 K. <sup>d</sup> Reference material (Dowex).

Table 3. Sulfur Content (wt %) for Dowex after Desulfonation Treatment at Different Reaction Time and pH Values<sup>a</sup>

pH	time (h)		
	2	4	6
1	0.60	0.84	0.39
3	0.64	1.17	0.43
4	0.57	0.62	0.51

<sup>a</sup> The starting material was the same sample D of Tables 1 and 2 (initial sulfur content was 11.2%).

Table 4. Iodide and Sulfate Amounts in the Bunsen Solution without and with Polymer

	without polymer	with polymer
I <sup>-</sup> (mmol)	63.5	58.2
SO <sub>4</sub> <sup>=</sup> (mmol)	39.3	17.8

The efficiency of H<sub>2</sub>SO<sub>4</sub> recovery by polymer sulfonation was tested measuring the H<sub>2</sub>SO<sub>4</sub> amount in the HI phase by comparison with Bunsen reaction carried out in the absence of polymer. The Bunsen mixture, after the online sulfonation, was filtered, and the concentration of I<sup>-</sup> and SO<sub>4</sub><sup>=</sup> ions in the liquid HI phase were measured by ionic chromatography.

A 4.0 g portion of H<sub>2</sub>SO<sub>4</sub> was supplied to the sulfuric acid decomposer, kept at 1073 K, and 20 mL of water while 10 g of I<sub>2</sub> were added to the Bunsen reactor (see Figure 1). At the end of the reaction (discoloration of the solution), the amounts of SO<sub>4</sub><sup>=</sup> and I<sup>-</sup> ions were measured and the results reported in the following Table 4. As can be seen, the Bunsen solution contains HI at about 38 wt % both with polymer and without polymer. When the polymer is added, we obtain an acceptable reduction in the amount of sulfate. The sulfuric acid recovery is about 56%. This shows the role of the polymer in the sulfuric acid seizing.

To put to good use the proposal of sulfonation reaction in the sulfur–iodine cycle, we must invert the reaction and restore the polymer and the sulfuric acid so that the latter is available for the following thermal treatment.

The procedures for the desulfonation of sulfonated polymers have been studied since the middle of the last century. These processes can be triggered by fluxing the polymer with concentrated phosphoric acid at temperatures around 500 K,<sup>24–26</sup> or heating the sulfonated polymer with concentrated hydrochloric acid at 437 K for 3 h.<sup>27</sup> The desulfonation of various polymers may also be promoted by treatment with superheated steam (573 K).<sup>20</sup> Moreover, the loss of sulfonic acid groups in sulfonated polymer membranes may occur during annealing experiments at a temperature of 563 K.<sup>28</sup>

The desulfonation of our sulfonated polymer, S-PSDVB, and of the reference polymer, Dowex, was obtained by using acid conditions at a fixed temperature of 553 K (see the Experimental Section). The sulfur contents measured for the Dowex polymer are reported in Table 3. The data show a modest effect of pH and reaction time; nevertheless, the reduction of the sulfur content is relevant, demonstrating the effectiveness of the desulfonation procedure.

The decrease of sulfur content in S-PSDVB, prepared according to the conditions reported for sample B in Table 1, is less satisfactory. The sulfur content, after 4 h of desulfonation at 550 K and pH 4, is reduced from 6.8% to only 5.4%.

The greater difficulty encountered in desulfonation, as well as in sulfonation for PSDVB, could be related to structural features that render the aromatic moiety of the polymer less accessible to the reagent. The use of polymers with more accessible sites which should favor the entire sulfonation/desulfonation process is under investigation.

## Conclusions

The H<sub>2</sub>SO<sub>4</sub>/HI mixtures coming from the Bunsen reaction can be separated using the new approach which has been described in this paper. Our results demonstrate the ability of the PSDVB to immobilize the H<sub>2</sub>SO<sub>4</sub> to form an insoluble phase of S-PSDVB that, after simple separation from HI, is able to restore, in part, the original acid and polymer.

This new method should allow a reduction of the water requests for the Bunsen reaction and limit the iodine content to the stoichiometric amount.

The results show an acceptable sulfuric acid recovery of about 56% with respect to the total SO<sub>2</sub> injected into the Bunsen reaction. The optimum conditions to carry out the capture reaction by polymer sulfonation are at present still being investigated.

The use of more active polymers to undergo an aromatic electrophilic substitution will improve the performance of the proposed method, in particular in terms of sulfonation and desulfonation efficiencies thus increasing the sulfonation degree of the polymer and the sulfuric acid recovery capacity and decreasing the desulfonation reaction time.

The effect of the introduction of this alternative route in the sulfur–iodine thermochemical cycle flow sheet is being studied and will be reported in a future paper.

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