RSC Advances

ROYAL SOCIETY
OF **CHEMISTRY**

www.rsc.org/advances

Green Chemistry RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/greenchem

Integrated desulfurization of diesel by combination of metal-free oxidation and product removal by molecularly imprinted polymers

Joana P. Ferreira,[a] Raquel Viveiros,[b] Anita Lourenço,[b] Mara Soares da Silva,[b] Andreia Rosatella,[a] Teresa Casimiro*[b] and Carlos A. M. Afonso*[a]

The production of ultra-low-sulfur diesel is an important worldwide demand. In this work a novel integrated method for desulfurization of diesel is proposed based on the combination of Brønsted acid catalyzed oxidation and the selective removal of the oxidized products using a molecularly imprinted polymer (MIP) produced in supercritical carbon dioxide (scCO$_2$). The biphasic oxidation reaction of dibenzothiophene sulfone (DBT), as model substrate, and H_2O_2 as oxidant, was optimized by testing different acid catalysts, and also different phase transfer catalysts (PTC), including two different ionic liquids (ILs) trihexyl(tetradecyl)phosphoniumchloride [$P_{6,6,6,14}$]Cl and Aliquat®. The products of the efficient oxidation of DBT, dibenzothiophene sulfoxide (DBTSO) and dibenzothiophene sulfone (DBTSO$_2$), were then selectively removed from real diesel using the MIP material with molecular recognition to DBTSO$_2$.

Introduction

Petroleum is a fossil fuel with numerous organic compounds with small amounts of nitrogen, oxygen, sulfur and metal ions. Some of these compounds, especially sulfur containing ones, are not favourable since their combustion leads to the release of SO$_x$ and other oxides, increasing atmospheric pollution. Therefore, good desulfurization processes are of high importance in petroleum and fuels processing, and a range of approaches have been reported concerning this issue. The main method to remove sulfur compounds from fuels is the hydrodesulfurization, that subjects the oil to high pressure and temperature in the presence of hydrogen and usually a metal catalyst,[1] resulting hydrogen sulphide as by-product. Hydrodesulfurization is effective in removing less hindered sulfur compounds however, it is inefficient in the removal of benzothiophenes and dibenzothiophenes from heavier fractions of petroleum.[2]

Other desulfurization processes have been reported, such as using biological systems to oxidize sulfur compounds (bio-desulfurization),[1-5] or using a reactive or non-destructive adsorption system.[1] Oxidative desulfurization is currently the most studied process to remove sulfur compounds from fuel. This method involves the modification of physical and chemical properties (e.g., change in solubility), improving the last step of separation of oxidized compounds. Initially, the reported oxidative processes involved the use of nitric oxides as oxidizing agents.[6] However, with the growing environmental awareness, emerging studies started to be more sustainable, using organic or hydro-peroxides as oxidants.[7-14] A more recent methodology to remove sulfur compounds from fuels is based on the use of selective two-phase extraction, such as ionic liquids (ILs) as phase-transfer promoters and receiving phase, i.e., triggering the molecules to move from diesel phase to the IL, where the oxidation reaction takes place.[15] In the oxidative approach the second important step is the efficient removal of oxidized products from the diesel, namely by precipitation and/or extraction. Yet this approach has some drawbacks such the final fuel contamination by IL and the difficult and incomplete removal of the oxidation products from diesel.

Molecular imprinted polymers (MIPs) are cross-linked polymers formed in the presence of a template, molecule for which the affinity is wanted. During the process the template forms a stable complex with the functional monomer(s), in the presence of a porogen and a cross-linker that freezes the complex within a rigid porous polymer matrix.[16] At the end, the template is removed leaving within the three-dimensional network, specific sites complementary to the template in size and functionality. These affinity materials have been successfully applied in several areas, as recently reviewed in literature.[17] MIPs have high potential because they mimic the affinity of natural materials, but they are very robust to extreme pH, temperature and pressure conditions and to organic solvents. Some drawbacks for their broad use are the intensive use of organic solvents, multi-step preparation with typical grinding and sieving of the synthesized polymers. Recently the development of MIPs using supercritical fluid technology have been proposed[18] and since then several applications have been reported.[19-22] The use of supercritical carbon dioxide (scCO$_2$) has shown to be an excellent alternative since MIPs are obtained ready-to-use as dry powders, with no need

---

[a] *Instituto de Investigação do Medicamento (iMed.ULisboa), Faculty of Pharmacy, University of Lisbon, Av. Prof. Gama Pinto, 1649-003, Lisboa, Portugal E-mail: carlosafonso@ff.ulisboa.pt*

[b] *REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal. E-mail: teresa.casimiro@fct.unl.pt.*

†Electronic supplementary information (ESI) available. See DOI: XXX

of further drying or mechanical steps. The powder is very homogeneous and easily packed into columns.[23] The high diffusivity and low viscosity of $scCO_2$ decreases the mass transfer limitations found in both conventional synthesis and template desorption. [24] In addition CO_2 is cheap, non-toxic, non-flammable, can be removed by simple depressurization and re-used thus replacing the use of organic solvents and leaving no residues in the MIP.

MIPs have been applied to the removal of benzothiophene (DBT)-based compounds from diesel and/or model oil (e.g. hexane, *n*-octane or acetonitrile). For example dibenzothiophene sulfone ($DBTSO_2$)-imprinted chitosan hydrogel proved to be selective in the absorption of $DBTSO_2$ from an acetonitrile solution when compared to other organosulfur compounds found in diesel. [25]A similar test was performed more recently, also using molecularly imprinted chitosan, showing that the MIP could be used to selectively adsorb organosulfurs from gasoline.[26]Another approach to molecular imprinting, was the preparation of surface-imprinted polymers using titanium dioxide[27] or potassium tetratitanate whisker ($K_2Ti_4O_9$)[28] as support, that presented some imprinting effects. However the adsorption tests in both studies were performed in model oil (*n*-octane) and not in real gasoline or diesel. Some recent examples also explored the use of other solid support surfaces namely carbon microspheres,[29] silica nanoparticles,[30] magnetic particles[31] and double-template MIP on the surface of carbon microspheres[32] and graphene oxide hybrids for[33] for selective absorption of DBT dissolved in fuel and/or in *n*-alkane. Cross-linked chitosan microspheres and electrospun chitosan nanofibers were recently applied for $DBTO_2$ removal from diesel.[34] A recent review by Liu *et al.* provides an overview on the use of MIP for deep desulfurization of fuel oils.[35]

Herein we propose an integrated method for desulfurization of diesel comprising two steps: 1) Free-metal oxidation of DBT into oxidized products (Fig. 1), and 2) Selective removal of the oxidized species using a MIP prepared using $scCO_2$.

We take advantage of the fact that *p*-toluenesulfonic acid (*p*-TsOH) is an efficient catalyst for the dihydroxylation of olefins using hydrogen peroxide[36] in combination with a clean method for the development of an easy-to-make and ready-to-use MIP with molecular recognition for the oxidized products. These prompted us to achieve an integrated, more efficient and mild process for the removal of more demanding benzothiophene-based compounds from diesel, by non-metal sulfur oxidation using hydrogen peroxide, followed by a MIP-selective removal of the products from diesel.

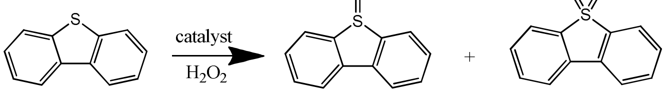


Fig. 1 Oxidation of dibenzothiophene (DBT) to dibenzothiophene sulfoxide (DBTSO) and dibenzothiophene sulfone ($DBTSO_2$).

Results and discussion

The two-phase oxidation of dibenzothiophene (DBT), as model of related benzothiophenes and dibenzothiophenes, by aqueous H_2O_2 and using *p*-TsOH as catalyst, was explored in hexane, dicholoroethene and diesel. Under different conditions such as temperature (RT to 80 ºC) and catalyst loading (10 to 50 mol%) only modest oxidation conversion was observed by GLC (see ESI†) and the maximum conversion of 39 % was obtained at 65 ºC using 30 mol% of *p*-TsOH (Table 1, entry 1).

The use of ionic liquids (ILs) as co-solvents has been demonstrated to increase the efficiency of different catalytic systems and oxidations. These compounds are also reported as efficient extractors of sulfur compounds from diesel.[1,2] Thus, two different ILs (trihexyl(tetradecyl)phosphoniumchloride $[P_{6,6,6,14}]Cl$ and Aliquat®) where tested as co-solvent, also acting as phase-transfer catalyst (PTC). Table 1 shows data for the oxidation of DBT to DBTSO and $DBTSO_2$ in model oil and diesel using ILs. The addition of ILs provided conversions above 94 % either in hexane (entries 2-4), dichloroethane (DCE) (entries 5 and 6) or diesel (entry 7). Interestingly, in diesel there was an increase on the $DBTSO_2$/DBTSO ratio (entries 2-6 *vs* entry 7).

Table 1 Selection of experiments for the oxidation of DBT to DBTSO and $DBTSO_2$ in model oil and diesel[a]

	IL(g)	Solvent	T (ºC)	Conv. DBTSO (%)[b]	Conv. $DBTSO_2$ (%)[b]	Total conv. (%)[b]
1	-	hexane	60	0	39.0	39.0
2	Aliquat® (1.1)	hexane	50	88.6	8.8	97.4
3	$[P_{6,6,6,14}]Cl$ (1.1)	hexane	50	86.3	8.1	94.4
4	Aliquat® (1.1)	hexane	65	87.8	11.0	98.8
5	Aliquat® (0.27)	DCE	65	79.7	19.3	99.0
6	$[P_{6,6,6,14}]Cl$ (0.26)	DCE	65	83.8	12.8	96.6
7	Aliquat® (0.26)	diesel	50	63.1	35.8	98.9

[a] General procedure: DBT (entry 1: 1.35 mmol; entries 2-7: 2.71 mmol) was dissolved in the solvent (entry 1: 6 mL; entries 2-7: 3 mL) and added to a solution of H_2O_2 (4 equivalents) and *p*-TsOH (30 mol%), followed by the addition of the IL, for 24 hours (except entry 4, 48 h), in a closed reactor. [b] Observed conversion by GLC to dibenzothiophene sulfoxide (DBTSO), dibenzothiophene sulfone ($DBTSO_2$) and total conversion (DBTSO + $DBTSO_2$). A complete list of experiments is provided at SI.

Despite all the known advantages, the use of ILs shows disadvantages for industrial applications derived from the high cost of the IL, potential final IL contamination of the diesel and the need of further removal of the oxidized products from the IL phase in order to enable the desirable IL reuse. With the purpose of circumvent these limitations we explored the use of the acid catalyst/aqueous H_2O_2 system in diesel without any co-solvent or at least using a PTC. The experiments, summarized in Table 2, were performed using real diesel by monitoring the DBT, DBTSO and $DBTSO_2$ present in diesel (5 mg/mL) at optimized conditions. The observed yields were determined by previous removal of the main diesel constituents by absorbing DBT, DBTSO and $DBTSO_2$ in silica followed by HPLC quantification (see ESI†).

In the absence of any PTC different acids were tested, such as *p*-TsOH, camphorsulfonic acid, dodecyl benzene sulfonic acid, formic acid, phosphoric acid and amberlyst®. Apart of *p*-TsOH (entry 1 of Table 2, 21.1 %), all the others provided lower yields (7-17%, entries 2-6) and in the absence of catalyst an even lower yield of oxidized product was observed (1.8 %, entry 7). Several potential PTCs were also tested namely Aliquat® (entry 8), CHAPS (entry 10) and sodium dodecylsulfonate (SDS, entry 11). Only SDS provided slightly better yields (29.1 %, entry 11) than in the absence of PTC (21.1 %, entry 1), and in general the sulfone ($DBTSO_2$) is the predominant product. The use of an higher excess of H_2O_2 (8 eq.) which was either added at once in one experiment or when H_2O_2 (4 eq.) were added followed by another 4 eq 24 hours after and *p*-TsOH (30 mol%) provided better results, respectively 25.5 % and 29.7 % (Table 2, entries 13 and 12). Those results suggest that the occurrence of competitive H_2O_2 decomposition plays an important role in the product formation.

Table 2 Effect of the catalyst and PTCs for the oxidation of DBT in diesel.[a]

	Catalyst (30 mol%)	PTC (30 mol%)	$DBTSO_2$ (%)[b]	DBTSO (%)[b]	η (%)[b]
1	*p*-TsOH	---	16.1	5.0	21.1
2	Camphor-sulfonic acid	---	9.3	5.6	14.9
3	dodecyl benzene sulfonic acid	---	8.7	8.1	16.8
4	Formic acid	---	0.8	6.2	7.0
5	Phosphoric acid	---	5.6	4.4	10.0
6	Amberlyst	---	12.8	3.8	16.6
7	---	---	1.8	0	1.8
8	*p*-TsOH	Aliquat®	13.1	8.1	21.2
9	*p*-TsOH	$[P_{6,6,6,14}]Cl$	11.0	10.4	21.4
10	*p*-TsOH	CHAPS	18.8	1.6	20.4
11	*p*-TsOH	SDS	24.9	4.2	29.1
12[c]	*p*-TsOH	---	24.9	4.8	29.7
13[d]	*p*-TsOH	---	16.7	8.8	25.5

[a] General procedure: DBT (50.0 mg, 0.27 mmol) was dissolved in diesel (10 mL), and added to a solution of H_2O_2 (4 equivalents), 30 mol% of catalyst, and 30 mol% of phase-transfer catalyst (PTC) , then stirred for 24 hours at 60 ºC, in a closed reactor. [b] Observed yield by HPLC of $DBTSO_2$, DBTSO and total ($DBTSO_2$ + DBTSO), average of two independent analysis. [c]After 24 h, more H_2O_2 (4 eq.), *p*-TsOH (30 mol%) were added and the reaction was continued for more 24 h. (total time of 48 h). [d] H_2O_2 was used (8 equivalents).

After this study on the acid catalyzed oxidation of DBT in diesel, the selective removal of the oxidized products from the diesel was explored using a MIP synthesized in $scCO_2$ using $DBTSO_2$ as template. Three different MIPs were synthesized based on MAA (methacrylic acid) 2-vinylpyridine (2Vpy) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) as functional monomers, and EGDMA (ethylene glycol dimethacrylate). (See ESI†) Preliminary binding studies showed that MAA based MIP presented the best recognition ability for $DBTSO_2$.

The MIP and the corresponding non-imprinted polymer (NIP) were loaded into a glass column (ID 1 x L20 cm). The following procedure was followed: 1) diesel was passed through the column; 2) the polymer was washed with hexane to remove the non-retained $DBTSO_2$; 3) acetonitrile was passed to remove the retained $DBTSO_2$. Samples were analysed by HPLC and the results are shown in Table 3.

MIP revealed higher affinity to $DBTSO_2$ than NIP (177 mg /g MIP; 47.2 % *vs* 136.5 mg /g NIP; 36.4 %, entry 1 *vs* entry 2). In addition, the observed purity of retained $DBTSO_2$ is higher for MIP (see ESI†). When lower amount of $DBTSO_2$ was passed through the MIP (although with the same concentration), higher percentage of $DBTSO_2$ was retained (69.9 % vs 47.2 %, entry 4 *vs* entry 1, Table 3) although with lower loading (105 mg /g MIP, entry 4). In addition, the reusability of the MIP was tested by performing three consecutive runs using fresh diesel solutions containing $DBTSO_2$. Interestingly the retained capability increased with the reuse (1st run: 41.8 %, 2nd run: 43.7 %, 3rd run: 47.5 %, entries 5-7, Table 3) but the final amount that the structure can recognize decreases which is probably due to the combination of the retained performance of the polymer and the increase of the polymer compaction inside the column, as it was observed an increase of the column head pressure. We should also mention that the MIP loading capability of 177 mg ($DBTSO_2$/g MIP) is considerable higher than the one reported recently for $DBTO_2$(4.2 mg $DBTO_2$/g MIP,[34]) and for DBT namely 20 mg DBT/g MIP,[30] 22.7 mg DBT/g MIP,[37] 88.8 mg DBT / g MIP,[29] 67.2 mg DBT / g MIP,[32] and in the same range as using graphene oxide (181.9 mg DBT/g MIP.[33]

Table 3 Observed binding of $DBTSO_2$ in diesel by MIP and NIP.[a]

	$DBTSO_2$ (mg)	Diesel (mL)	$DBTSO_2$ retained[b] (%)	$DBTSO_2$/pol (mg/g)
1	75.4	15	47.2	177.0
2	75.6	15	36.4	136.5
3	50.0	10	56.7	141.5
4	30.0	6	69.9	105.0
5	75.4	15	41.8	156.5
6[c]	75.0	15	43.7	164.0
7[c]	75.1	15	47.5	178.0

[a] Diesel containing $DBTSO_2$ (23.1 mM) was passed through a glass column loaded with polymer (200 mg), then washed successively with hexane and acetonitrile. In all entries MIP was used except entry 2 where NIP was used. [b]$DBTSO_2$retained by the polymer that was present in the acetonitrile fraction as determined by HPLC (duplicate analysis). [c] Observed results of reused MIP from the previously experiment.

Finally, the integrated process of the organocatalyzed DBT oxidation and removal of the oxidized product in diesel by the synthesised MIP was tested. DBT (50 mg) was dissolved in diesel (10 mL), the oxidation step was performed (H_2O_2 (4 eq.), *p*-TsOH (30 mol%), 60 ºC, 24 h), the diesel phase was decanted and passed through a MIP packed column (200 mg), allowing the removal of 10.8 % of oxidized $DBTSO_2$. This result is comparable to the expected overall yield of 12 % derived from the combination of the oxidation step (21.1 %, Table 2, entry 1) and binding step (56.7 %, Table 3, entry 3).

Conclusions

In conclusion, this work describes a novel integrated process for the desulfurization of diesel that provides the following key features: 1) No metal catalysis or co-solvent (e.g. ionic liquids) are required, which avoids undesirable contamination of the desulfurized diesel; 2) it requires a readily available catalyst (*p*-TsOH) as well as a desirable oxidant (aqueous H_2O_2) that forms only water as side product; 3) Synthesis of MIP with affinity to $DBTSO_2$ was successfully achieved using a $scCO_2$-assisted clean process yielding ready-to-use powders without using organic solvents and without the need of time consuming polymer crushing and sieving; 4) MAA-based MIP showed the best performance in selectivity binding of the oxidized product in diesel as well as in further removal and reuse of the MIP.

These observed features of the integrated system, only moderately optimized in this study, prompt us to believe that it has the appropriate important requirements for further optimization for large scale application not only for the desulfurization of diesel but also for gasoline.

Experimental

General procedure for the synthesis of the MIP material in $scCO_2$

MIPs were synthesized in $scCO_2$ using a high pressure apparatus already described elsewhere.[38] (see ESI†) In a typical polymerization methacrylic acid (MAA) was used as functional monomer, EGDMA as cross-linker, AIBN as initiator and $DBTSO_2$ as template, with a molar ratio of monomer/template/cross-linker of 1:5:25. The MIP was obtained as a dry, white, free flowing powder, ready to be packed in the glass column.

General procedure for the integrated oxidation of dibenzothiophene (DBT) followed by $DBTSO_2$ removal using MIP

To a solution of 50 mg of dibenzothiophene (DBT) in 10 mL of diesel was added a solution of 30 mol% of *p*-TsOH in 4 equivalents of H_2O_2. After 24 hours at 60ºC, the reaction mixture was passed through the glass column containing the MIP (200 mg), and dragged with hexane followed by acetonitrile to remove binding compounds from the polymer. The acetonitrile fraction was analysed by HPLC providing 12.7 mg of $DBTSO_2$ (10.8%).

Acknowledgements

The authors are grateful to Fundação para a Ciência e Tecnologia (FCT-Lisbon), FSE and FEDER for financial support through projects PTDC/QUI-QUI/102460/2008, PEst-OE/SAU/UI4013/2011, PTDC/QEQ-PRS/2757/2012 and PEst-C/EQB/LA0006/2013. RV acknowledges FCT-Lisbon and Hovione for BDE doctoral grant SFRH/BDE/51907/2012.

References

1. P. S. Kulkarni and C. A. M. Afonso, *Green Chem.*, 2010, **12**, 1139-1149.
2 V.C. Srivastava, *RSC Advances*, 2012, **2**, 759-783.
3 J. Pan, F. Wu, J. Wang, L. Yu, N. H. Khayyat, B. C. Stark and J. J. Kilbane, *Fuel*, 2013, **112**, 385-390.
4 A. A. Nuhu, *Reviews in Environmental Science and BioTechnology*, 2013, **12**, 9-23.
5 P. R. Patwardhan, M. T. Timko, C. A. Class, R. E. Bonomi, Y. Kida, H. H. Hernandez, J. W. Tester, and W. H. Green, *Energy Fuels,* 2013, **27,** 6108−6117.
6 P. S. Tam, J. R. Kittrell and J. W. Eldridge, *Ind. Eng. Chem. Res.*, 1990, **29**, 321-324.
7 M. T. Timko, E. Schmois, P. Patwardhan, Y. Kida, C. A. Class, W. H. Green, R. K. Nelson, and C. M. Reddy, *Energy Fuels,* 2014, **28,** 2977−2983.
8 K. Sato, M. Hyodo, M. Aoki, X. Q. Zheng and R. Noyori, *Tetrahedron*, 2001, **57**, 2469-2476.
9 W. Al-Maksoud, S. Daniele and A. B. Sorokin, *Green Chem.*, 2008, **10**, 447.
10 Z. Juan, Z. Dishun, Y. Liyan and L. Yongbo, *Chem. Eng. J.*, 2010, **156**, 528-531.
11 Y. Shiraishi, T. Naito and T. Hirai, *Ind. Eng. Chem. Res.*, 2003, **42**, 6034-6039.
12 L. C. Caero, E. Hernández, F. Pedraza and F. Murrieta, *Catal Today*, 2005, **107-108**, 564-569.
13 A. K. Vardhaman, S. Sikdar and C. V. Sastri, *Indian J Chem A*, 2011, **50**, 427-431.
14 S. K. Karmee, L. Greiner, A. Kraynov, T. E. Muller, B. Niemeijer and W. Leitner, *Chem Commun.*, 2010, **46**, 6705-6707.
15 D. Zhao, Y. Wang, E. Duan and J. Zhang, *Fuel Process. Technol.*, 2010, **91**, 1803-1806.
16 E. Turiel, A. Martín-Esteban, *J. Sep. Sc.*, 2009, **19**, 3278-3284.
17 M. J. Whitcombe, N. Kirschb and I A. Nicholls, *J. Mol. Recognit.*, 2014, **27**, 297-401.
18 A. R. C. Duarte, T. Casimiro, A. Aguiar-Ricardo, A. Luísa Simplício and C.M. M. Duarte, *J. Supercrit. Fluids*, 2006, **39**, 102-106.
19 L. Ye, K. Yoshimasu, D. Kolodziej, J.D.C. Francisco and E.S. Dey, *J. Appl. Polym. Sc.* 2006, **102**, 2863–2867.
20 M. Soares da Silva, R. Viveiros, V. D. B. Bonifácio, A. Aguiar-Ricardo, T. Casimiro, *RSC Adv.*, 2012, **2**, 5075-5079.
21 M. Soares da Silva, R. Viveiros, M. B. Coelho, A. Aguiar-Ricardo, T. Casimiro, *Chem. Eng. Sc.*, 2012, **68**, 94-100.
22 M. Soares da Silva, F. L. Nobrega, A. Aguiar-Ricardo, E.J. Cabrita and T. Casimiro, *J. Supercrit. Fluids*, 2011, **58**, 150-157.
23 M. Soares da Silva, E.R. Vão, M. Temtem, L. Mafra, J. Caldeira, A. Aguiar-Ricardo and T. Casimiro, *Bios. Bioelectr.*, 2010, **25**, 1742-1747.
24 A. Ellwanger, C. Berggren, S. Bayoudh, C. Crecenzi, L. Karlsson, P.K. Owens, K. Ensing, P. Cormack, D. Sherrington and B. Sellergren, *Analyst*, 2001, **126**, 784-792.
25 J. Aburto and S. Le Borgne, *Macromolecules*, 2004, **37**, 2938-2943.
26 Y. Chang, L. Zhang, H. Ying, Z. Li, H. Lv and P. Ouyang, *Appl. Biochem. Biotechnol.*, 2010, **160**, 593-603.
27 P. Xu, W. Xu, X. Zhang and Y. Yan, *Microchim. Acta*, 2010, **171**, 441-449.
28 W. Z. Xu, W. Zhou, L. H. Bian, W. H. Huang and X. Y. Wu, *J. Sep. Sci.*, 2011, **34**, 1746-1753.
29 W. Liu, H. Zhao, Y. Yang, X. Liu and B. Xu, *Appl. Surf. Sci.*, 2013, **277**, 146-154.
30 W. Yang, L. Liu, Z. Zhou, H. Liu, B. Xie and W. Xu, *Appl. Surf. Sci.*, 2013, **282**, 809-819.
31 H. Li, W. Xu, N. Wang, X. Ma, D. Niu, B. Jiang, L. Liu, W. Huang, W. Yang and Z. Zhou, *Microchim. Acta*, 2012, **179**, 123-130.
32 W. Liu, X. Liu, Y. Yang, Y. Zhang, B. Xu, *Fuel,* 2014, **117,** 184-190.
33 F. Duan, C. Chen, G. Wang, Y. Yang, X. Liu, Y. Qin, *RSC Adv.,* 2014, **4,** 1469-1475.
34 A. S. Ogunlaja, M. J. Coombes, N. Torto, Z. R. Tshentu, *Reactive & Functional Polymers,* 2014, **81,** 61-76.
35 Y. Yang, X.Liu, B.Xu, *New Carbon Materials,* 2014, **29,** 1-14.
36 A. A. Rosatella and C. A. M. Afonso, *Adv. Synth. Catal.*, 2011, **353**, 2920-2926.
37 Y. Chang, L. Zhang, H. Ying, Z. Li, H. Lv and P. Ouyang, *Appl. Biochem. Biotechnol.*, 2010, **160**, 593-603.
38 T. Casimiro, A.M. Banet-Osuna, M. Nunes da Ponte and A. Aguiar-Ricardo, *Eur. Polym. J.* 2005, **41**, 1947-1953.

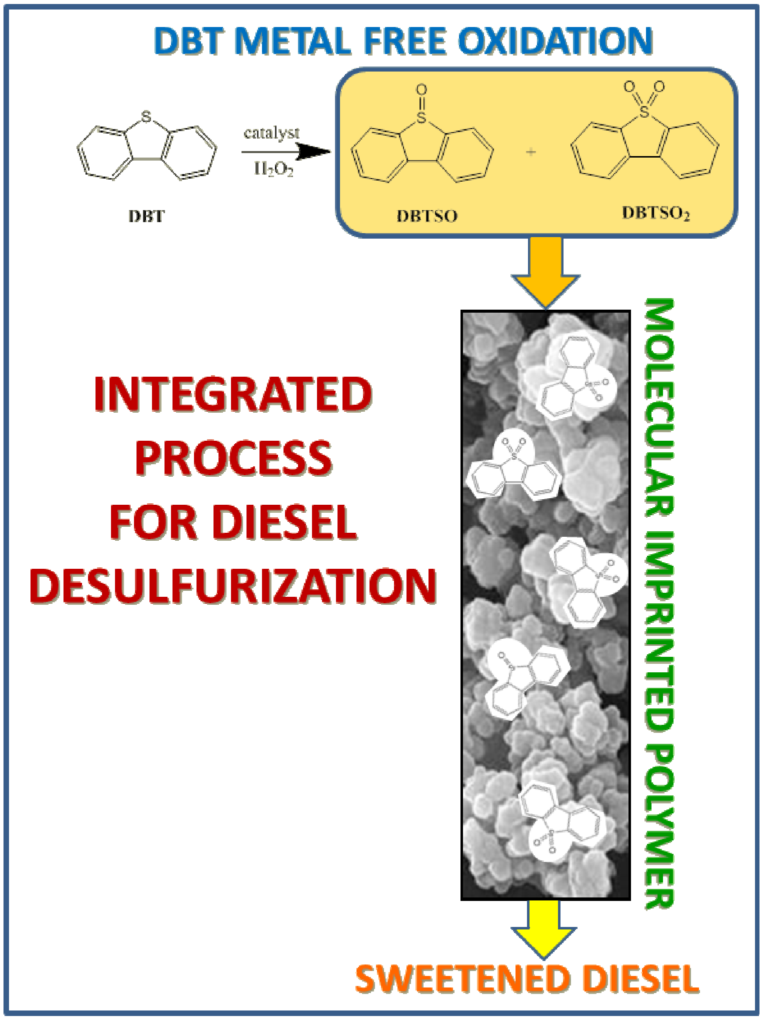
Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Integrated desulfurization of diesel by combination of metal-free oxidation and product removal by molecularly imprinted polymers

Joana P. Ferreira,[a] Raquel Viveiros,[b] Anita Lourenço,[b] Mara Soares da Silva,[b] Andreia Rosatella,[a] Teresa Casimiro*[b] and Carlos A. M. Afonso*[a]



The desulfurization of diesel of the more reluctant compound dibenzothiophene sulfone (DBTSO$_2$) is achieved based on the combination of Brønsted acid catalyzed oxidation of dibenzothiophene sulfone (DBT) by H_2O_2 and the selective removal of the oxidized products using a molecularly imprinted polymer (MIP) produced in supercritical carbon dioxide (scCO$_2$).