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### Adsorptive Desulfurisation of Diesel by Modified Carbons

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#### ABSTRACT

The regulation on sulfur in diesel has become stringent and the maximum sulfur content in diesel is reduced to less than 15 ppmw in U.S from 2006. In India also, the sulfur specification is gradually made stringent and will be introducing Bharat Stage IV norm of 50 ppm sulfur by 2010 in select metros and BS III norm of 350 ppm in rest of India. The Hydrodesulphurisation units which were implemented in many refineries in India during 2000 are being revamped to meet the new norms. Alternate methods of desulfurisation of diesel is being explored worldwide in view of the increasing severity of Diesel HDS units required to meet the specifications. The increased severity is mainly due to the presence of refractory sulfur compounds in the last few hundred ppms of sulfur in diesel fuel. The most difficult sulfur compound namely 4,6 Dimethyl Dibenzothiophene is present in > 100 ppm in many diesel fuels. The alternate method of desulfurisation which are extensively reported are Oxidative desulfurisation and Adsorptive desulfurisation. The oxidative desulfurisation is very selective in converting the refractory sulfur compounds to sulfones but suffers from a disadvantage of using an expensive oxidant and further using an extraction process for removal of sulfones which is energy intensive. The Adsorptive desulfurisation using zeolite as adsorbent looks less attractive option as it requires hydrogen for producing fuels meeting Euro III/ IV norms. In the present study we report our results obtained on Adsorptive desulfurisation of SR diesel from a low sulfur crude using Modified Activated Carbons.

The Activated Carbons obtained from different commercial sources were used in the study. Suitable modification procedures were employed to increase the surface area of the carbon materials and also to introduce surface functional groups which can modify the adsorption characteristics of carbon materials. The adsorbent was extensively characterized before and after modifications using FT- IR, XRD, BET-sorptometry and scanning electron microscopic techniques.

The studies on adsorbent were carried out using SR diesel from our Cauvery Basin Refinery Distillation unit. The SR diesel was characterized using GC-PFPD unit for analyzing the type of sulfur compounds present in the fraction.

The adsorption studies were carried out in laboratory using 5/10 gms of the adsorbent and the sulfur removal was monitored continuously. The studies were also carried out at 100 gms level of the adsorbent. The regeneration of the adsorbent saturated with sulfur compounds was also studied in detail. Solvent regeneration using toluene was found to be effective in reusing the adsorbent. The studies indicate that adsorbents (activated carbons) suitably modified can remove refractory sulphur compounds from diesel fuel. Further the studies confirmed that the adsorbent is regenerable to sustain its adsorptivity for sulphur compounds in diesel.

These studies have also been extended to carbon material generated from natural sources and the results obtained are comparable with those obtained with carbon obtained from commercial sources.

#### **KEYWORDS**

#### INTRODUCTION

Removal of organo sulphur compounds from diesel is an issue of concern from scientific, social, economic and environmental view points. Any break through achieved in desulphurization technology will have its impact on human well being. Burning of fuel (gasoline or diesel) with S contents beyond permissible limits cause ill effects on human health. Current world demands zero sulphur fuel. Production of clean fuel has always been the goal of petroleum refining industry. But refinery itself in engulfed now in the vicious circle of a host of problems that include environmental legislation, crude oil variation, product demand, economic imbalances, energy uptake, safety and process efficiency. It should not be mistaken that conventional HDS

can be a panacea to the recurring problem of S specification in the transportation fuels. Newer technologies, if found promising, should be given place.

The uniqueness of the present work is that unlike the severe conditions of operation which are inevitable in the conventional hydrodesulphurization process, the current experimentation aims at developing the desulphurisation process under modest conditions of temperature (room temperature) and pressure (atmospheric pressure). The process is based on selective adsorption of organo sulphur compounds onto the tailored carbon surfaces which are used as adsorbents.

#### EXPERIMENTAL

#### ADSORPTIVE DESULPHURISATION

#### ADSORBENTS FOR DESULPHURIZATION

Several commercially available activated carbon materials of varying physical and chemical properties were tested as adsorbents for the removal of organo sulphur compounds from SR diesel from our Cauvery Basin Refinery Distillation unit. Among them, adsorbent carbon was purchased from adsorbent Carbons Pvt. Ltd., Tuticorn. Calgon carbon was purchased from Calgon Carbon (Tianjin) Co. Ltd., Activated carbons, IG 18 x 40, IG 12 x 40 and IG 8 x 30 were purchased from Indo German Carbon Ltd., Kerala. Activated carbons, AC 4 x 8, AC 6 x 12, AC 12 x 30 were purchased from Active Carbon Pvt. Ltd., Hyderabad. In addition to the afore mentioned commercially available carbons, two high specific surface area, microporous and hydrophilic activated carbon materials possessing were produced from botanical sources. The details of the methods of preparation, characterization and applications can be found in [1].

#### SULPHUR ADSORPTION

The potential of the afore mentioned carbon materials was tested. In a typical experiment the glass column of length 50 cm and internal diameter 1.5 cm is packed with 5.0 g of sorbent carbon column with glass beads on either sides. Deisel is fed on to the sorbent bed in the column through a burette at the slowest flow rate possible. The first 20 ml product collected at the bottom of the column (out let) was analyzed for S. From the S content remaining in the product and subtracting the same from the S content in the feed diesel (737 ppm), the S content adsorbed (removed) by the carbon sorbent is obtained. Lower the S content in the product obtained through the sorbent column, higher is the sorption capacity of the activated carbon under test. The carbon materials are thus screened. Adsorbent carbon and Calgon carbon showed outstanding performance for the adsorption of S compounds in the SR diesel. So further studies on activation, desulphurization and regeneration were only focused on Adsorbent carbon and Calgon carbon.

#### SULPHUR ANALYSIS

#### CARBON ACTIVATION METHODS

#### CONC. HNO<sub>3</sub> TREATMENT

Treatment with Conc.  $HNO_3$  changes the surface chemistry of carbon materials (2). Acid groups like carboxyl groups can be formed by  $HNO_3$  treatment (3). Such oxidative treatment aids the formation of several oxygen surface functional groups whose presence in most cases increases the adsorption capacity of carbon materials.

Treatment of carbon material (Calgon carbon as received and Adsorbent carbon as received) involve the following steps: The wt./wt. % ratio of carbon to Conc.  $HNO_3$  is maintained at 1:5. To 250 g Conc.  $HNO_3$  50 g carbon material (Adosorbent carbon or Calgon carbon) is added. The content are taken in a round bottom (RB) flask equipped with a thermometer to monitor the temperature. Also a magnetic pellet is placed in the RB flask to stir the contents thoroughly using a magnetic stirrer. The oxidative treatment of carbon with Conc.  $HNO_3$  is carried out at 60 °C for 2 h under refluxing conditions. After 2 h, the contents in the RB flask are cooled to room temperature, transferred into a sintered funnel and washed with excess distilled water dried at 110 °C for 2 h. Thus Conc.  $HNO_3$  treated adsorbent carbon are prepared.

#### ARGON ACTIVATION

Ar activation involves thermal activation of nitric acid treated carbon materials (adsorbent carbon as received and calgon carbon as received) at a temperature of 800 °C in Ar atmosphere. The nitric acid treated carbon material is placed in a cylindrical quartz tube. The quartz tube is sealed on either sides

preventing any air entering into the tube. The quartz tube is placed horizontally in a tubular furnace. Ar gas is allowed to flow through the quartz tube containing the carbon material to be activated. Required temperature of activation is set in the temperature controller connected to the furnace. The temperature of the furnace is raised at a heating rate of 20 °C/min. Once the temperature is reached to 800 °C, the sample is allowed to activate at that temperature in the flow of argon for 2 h after which the temperature of the furnace is brought to room temperature. The samples thus obtained are termed as nitric acid treated Ar activated carbon materials (either adsorbent carbon or calgon carbon).

#### **CHARACTERIZATION**

#### 1. XRD

X-ray diffraction patterns of carbon materials were recorded using a Rigaku Miniflex II desk top X-ray diffractometer operated at a scanning rate of 0.05 ° with CuK $\alpha$  radiation ( $\lambda$  = 154.178 pm) and a Ni filter. Diffraction profiles were obtained by the usual  $\theta$ -2 $\theta$  scan in the range of 5-70 °.

#### 2. BET-SORPTOMETRY

Nitrogen sorption isotherms were recorded using Sorptomatic 1990 Carlo Erba instrument at – 196 °C on adsorbent, modified adsorbent, calgon and modified calgon carbon materials. Prior to measurements the samples were degassed overnight at 250 °C under vacuum. High pure nitrogen was used as adsorbate at liquid nitrogen temperature.

#### 3. FT-IR

Fourier transform infrared spectra (FT-IR) were recorded on Shimadzu photometer. The spectra range of analysis is  $450 - 4000 \text{ cm}^{-1}$  with a resolution of 4 cm-1. The spectra were obtained in transmission mode at 20 scans. Pressed KBr pellets were prepared by grinding 200 mg of KBr with 0.5 g of carbon sample.

#### 4. SEM

High resolution scanning electron microscopy images of carbon materials were obtained using FEL, Model: Quanta 200 scanning electron microscope at two different magnifications namely 10, 000 x and 2000 x at a scanning voltage of 30 kV.

#### REGENERATION

#### **RESULTS AND DISCUSSION**

#### XRD

Details of phase structure of carbon materials are obtained from X-ray diffraction studies. X-ray diffraction patterns of adsorbent carbon as received, adsorbent carbon treated with conc.  $HNO_3$  and adsorbent carbon treated with  $HNO_3$  followed by subsequent activation in Ar atmosphere were shown in Figs. 1(a), 1 (b) and 1 (c) respectively. Two intense and broad diffraction peaks centered at 20 values of 25.4 and 43.4 were observed in adsorbent carbon as well as modified adsorbent carbons. The two afore mentioned peaks can be indexed to (002) and (101) planes of crystalline hexagonal graphite lattice respectively [(JCPDS-41-1487), (4)]

The phase structure of adsorbent carbon remained unaltered upon nitric acid treatment (Figs. 1 (a) and 1 (b)). But in the case of adsorbent carbon treated with nitric acid followed by activation in Ar atmosphere an additional intense and narrow diffraction peak is seen at  $2\theta = 26.7$  (Fig. 1(c)). This is attributed to (002) reflection from highly crystalline graphitic carbon [5]. Nitric acid treated Ar activated adsorbent carbon (Fig. 1 (c)) is more crystalline than either adsorbent carbon as received or adsorbent carbon treated with nitric acid alone. Thus Ar activation improved the crystallinity of nitric acid treated adsorbent carbon.



Fig. 1. XRD pattern of (a) Adsorbent carbon as received, (b) Adsorbent carbon treated with  $HNO_3$  and (c) Adsorbent carbon treated with  $HNO_3$  and activated with Ar



Fig. 2. XRD pattern of (a) Calgon carbon as received, (b) Calgon carbon treated with  $HNO_3$  and (c) Calgon carbon treated with  $HNO_3$  followed by Ar activation

X-ray diffraction patterns of calgon carbon as received, calgon carbon treated with  $HNO_3$  and calgon carbon treated with  $HNO_3$  followed by Ar activation were shown in Figs. 2 (a), (b) and (c) respectively. The diffraction peaks arising from each of the afore mentioned carbon samples were indexed and are typical of graphitic carbon structure (5).

Neither  $HNO_3$  treatment (Fig. 2 (b)) nor  $HNO_3$  treatment with subsequent Ar activation (Fig. 2 (c)) altered the structure of original calgon carbon sample (Fig. 2 (a)). Thus either  $HNO_3$  treatment or Ar activation has no effect on the phase structure of calgon carbon.

There is a marked difference in the structural order between adsorbent carbon and calgon carbon (Figs. 1 and 2). No diffraction peaks resulted from adsorbent carbon or modified adsorbent carbon beyond  $2\theta = 50^{\circ}$  (Fig. 1) in sharp contrast to the characteristic diffraction peaks resulting from calgon and modified calgon carbon above  $2\theta = 50^{\circ}$  Thus calgon based carbons are structurally more ordered than adsorbent based carbons.

#### 2. BET (Brunauer-Emmett-Teller) -SORPTOMETRY – PORE STRUCTURE ANALYSIS

Details of pore structure of carbon materials were obtained from  $N_2$  sorption studies.  $N_2$  adsorption-desorption isotherms of adsorbent carbon, modified adsorbent carbon, calgon carbon and modified calgon carbon are shown in Fig. 3,

The N<sub>2</sub> adsorption-desorption isotherms arising from adsorbent carbon as received (Fig. 3 (a)), HNO<sub>3</sub> treated adsorbent carbon (Fig. 3 (b)) and HNO<sub>3</sub> treated Ar activated adsorbent carbon (Fig. 3 (c)) are of typical type I isotherms in nature which are characteristic of microporous materials as per IUPAC classification (6).

The afore mentioned adsorption curves rose sharply at relative pressure upto 0.10. Beyond this value of P/P0 the isotherms presented a plateau with increasing relative pressure. Also the adsorption and desorption branches were parallel over a wide range at higher relative pressure. This is an indication of the narrow pore size distribution in microporous materials with slit-like or plate-like pores (7).

The shape of isotherms presented by calgon carbon as received (Fig. 3 (d)), calgon carbon treated with HNO<sub>3</sub> (Fig. 3 (e)) and calgon carbon treated with HNO<sub>3</sub> followed by Ar activation (Fig. 3 (f)) are distinctly different from the Type I isotherms resulted from adsorbent and modified adsorbent carbons (Figs. 3 (a), (b) and (c)). The isotherms resulting from calgon and modified calgon carbon samples are a combination of type I and type II isotherms. Such isotherms indicate pore structure which is a combination of micropores and mesopores. Presence of such mesopores in addition to micropores enhance the adsorption capacity for relatively large adsorbate molecules (8, 9).



Fig. 3. Nitrogen adsorption-desorption isotherms of (a) Adsorbent carbon as received, (b) Adsorbent carbon treated with  $HNO_3$ , (c) Adsorbent carbon treated with  $HNO_3$  followed by Ar activation, (d) Calgon carbon as received, (e) Calgon carbon treated with  $HNO_3$  and (f) Calgon carbon treated with  $HNO_3$  followed by Ar activation

The BET surface area values were deduced from the isotherm analysis in the relative pressure range of 0.04-0.20 asuming that the surface area occupied by per physisorbed nitrogen molecule as  $0.162 \text{ nm}^2$ . The total pore volume was calculated from the amount adsorbed (liquid volume of nitrogen) at a relative pressure of 0.99. The specific surface area values and the total pore volume values thus deduced are summarized in Table 1. Analysis of data in Table 1 reveal that irrespective of the parent carbon material, HNO<sub>3</sub> treatment essentially reduces special surface area values and the total pore volume. It is observed both in the case of adsorbent carbon as well as calgon carbon

that upon treatment with conc. HNO<sub>3</sub>, the surface area values which were originally 950 and 1014 m<sup>2</sup>/g were reduced to 882 and 649 m<sup>2</sup>/g respectively. Subsequent activation in Ar atmosphere at 800 °C for 2 h facilitated regaining of the original surface area values in the case of both adsorbent carbon and calgon carbon. Thus Ar activation is inevitable for keeping intact the original textural and porous characteristics of the carbon materials even after treatment with conc. HNO<sub>3</sub> which essentially results in loss of pore volume and in turn specific surface area values.

Table 1. Porosity characteristics of adsorbent, modified adsorbent, calgon and modified calgon carbon materials

Carbon sample	Specific Surface Area Values (m <sup>2</sup> /g)	Total Pore Volume (cm <sup>3</sup> /g)
Adsorbent carbon as received	950	0.451
Adsorbent carbon treated with Conc. HNO <sub>3</sub>	882	0.398
Adsorbent carbon treated with Conc. HNO <sub>3</sub> followed by Ar activation	1048	0.523
Calgon carbon as received	1014	0.587
Calgon carbon treated with Conc. HNO <sub>3</sub>	649	0.387
Calgon carbon treated with Conc. HNO <sub>3</sub> followed by Ar activation	996	0.598

#### FT-IR

Details of oxygen containing surface functional groups on the surface of carbon materials are obtained from FT-IR studies. The FT-IR spectra of adsorbent carbon as received, adsorbent carbon treated with  $HNO_3$  and adsorbent carbon treated with  $HNO_3$  followed by Ar activation are shown in Figs. 4 (a), (b) and (c) respectively.



#### Fig. 4. FT-IR

spectra of (a)

Adsorbent carbon as received, (b) Adsorbent carbon treated with HNO<sub>3</sub> and (c) Adsorbent carbon treated with HNO<sub>3</sub> and activated with Ar

The main distinguishing feature observed in the carbon samples after nitric acid treatment is the presence of shoulder at 1749 cm<sup>-1</sup> (Fig. 4 (b)). This is a result of stretching vibration of C=O bond in aldehydes, ketones, lactones or carboxyl groups. Thus upon nitric acid treatment C=O group is generated on the adsorbent carbon surface which is absent otherwise. Also the afore mentioned shoulder at 1749 cm<sup>-1</sup> became intense and developed in to sharp peak upon activation in Ar atmosphere (Fig. 4 (c)) (10, 11, 12).

But for this difference all the three samples showed similar but rich surface chemistry with a variety of oxygen containing functional groups. The following functional groups are common to adsorbent carbon as well as modified adsorbent carbon (Figs. 4 (a), (b) and (c)): A sharp band at 3738 cm<sup>-1</sup> is ascribed to isolated OH groups. A wide, intense band in the range of 3200-3600 cm-1 with a maximum at about 3440 cm-1 is assigned to the O-H stretching

mode of hydroxyl groups and adsorbed water (13). Two sharp, narrow and intense bands at 2922 and 2855 cm<sup>-1</sup> are a result of aliphatic C-H stretching in CH<sub>2</sub> (mythylene group) and CH<sub>3</sub> (methyl group) respectively. It is to note that the peak resulting from the asymmetric C-H stretching of methyl group is more intense that that arising from methylene group. A sharp intense peak at 1640 cm<sup>-1</sup> is attributed to the carbonyl groups in quinone. Broad bands observed in the range of 1300 - 1000 cm<sup>-1</sup> are attributed to C-O stretching in acids, alcohols, phenols, ethers and esters . Broad bands in the range of 600 - 800 cm<sup>-1</sup> are a result of the out of plane deformation mode of C-H in various substituted benzene rings (13, 8).

FT-IR spectra of calgon carbon as received, calgon carbon treated with Conc.  $HNO_3$  and calgon carbon treated with Conc.  $HNO_3$  followed by Ar activation are shown in Figs. 5 (a), (b) and (c) respectively. There are striking differences in the surface chemistry (functionality) among the afore mentioned samples. This indicate that each of the methods of activation, whether it be  $HNO_3$  treatment or Ar activation, has got a specific role to play and surface transformation to induce. Upon activation with Conc.  $HNO_3$  several new bands originated at wave numbers corresponding to 3790, 2305 and 1387 cm<sup>-1</sup> which can be attributed to isolated O-H groups, ketone surface groups (14) and the in-plane bending vibration of C-H in methyl group (15) respectively (Fig. 5 (b)). In addition to the generation of -OH, C=O and  $-CH_3$  groups, a broad featureless shoulder is observed in the range 2910-2990 cm<sup>-1</sup> which is a result of aliphatic C-H stretching in methylene and methyl groups.

Ar activation of Conc. HNO<sub>3</sub> treated calgon carbon induced certain specific changes in to the spectral features. The first and foremost change in the appearance of a broad shoulder at 1753 cm<sup>-1</sup> attributable to the origin of C=O group of carboxylic acid Fig. 5 (c). Also the broad featureless shoulder presented by HNO<sub>3</sub> treated calgon carbon in the range 2910-2990 cm<sup>-1</sup> developed into two clear sharp peaks centered at 2956 and 2918 cm<sup>-1</sup> which are attributed to the asymmetric stretching vibration of C-H in methyl and methylene groups indicating the fact that Ar activation results in the generation of CH<sub>2</sub>= and CH<sub>3</sub> type groups on the surface of calgon carbon which are other wise absent.

In spite of the several striking changes brought about, as discussed above, into the surface functionality of calgon carbon upon treatment with Conc.  $HNO_3$  and subsequent Ar activation, some inherent functional groups of parent calgon carbon remained unaltered even after modification. The spectral features common to all the three samples shown in Figs. 5 (a), (b) and (c) are as follows: the broad intense transmission peak centered at 3450 cm<sup>-1</sup> corresponding to OH stretching mode of hydroxyl groups and adsorbed water and the broad intense peak centered at 1075 cm<sup>-1</sup> which can be attributed to C-O stretching in acids, alcohols, phenols, ethers and esters (16).

Thus a variety of surface functional groups, namely, the hydrophilic groups such as C=O (carboxylic and ketonic), isolated -OH groups and hydrophobic groups such as  $CH_2$ = and  $CH_3$  were generated on the calgon carbon surface upon treatment with Conc. HNO<sub>3</sub> and subsequent activation in Ar atmosphere. Interestingly such a transformation in surface chemistry is achieved by keeping intact the inherent surface functionality of parent calgon carbon (Fig. 5 (a)).



Fig. 5. FT-IR spectra of (a) Calgon carbon as received, (b) Calgon carbon treated with  $HNO_3$  and (c) Calgon carbon treated with  $HNO_3$  followed by Ar activation

#### SEM

Details of surface microstructure of calgon carbon (as received) and adsorbent carbon (as received) are obtained from the scanning electronic microscopic studies. SEM images facilitate direct observation of the surface morphological features of adsobents. SEM images of calgon carbon as received at two different magnifications namely 10, 000 x and 2, 000 x are shown in Figs. 6 (a) and (b). The calgon carbon particles possess slate like morphology. The surface of calgon carbon is highly heterogeneous and rough with steps, kinks, edges and terraces.



Fig. 6. SEM images (a) calgon carbon as received (magnification - 10, 000 x), (b) calgon carbon as received (magnification - 2, 000 x), (c) adsorbent carbon as received (magnification - 10, 000 x) and (d) adsorbent carbon as received (magnification - 2,000 x)

SEM images of adsorbent carbon as received are recorded at two different magnifications namely 10, 000 x and 2000 x. The two afore mentioned images are depicted in Fig. 6 (c) and (d) respectively. There is close resemblance between the surface morphology of adsorbent carbon as received (Fig. 6 (c, d)) and calgon carbon as received (Fig. 6 (a, b)). Both the carbon materials possess slate like particle morphology. But the surface of adsorbent carbon (Fig. 6 (c)) is relatively smoother than that offered by calgon carbon (Fig. 6 (a)). Unlike calgon carbon surface (Fig. 6 (a)), some porous network which in its incipient stage is seen on the surface of adsorbent carbon (Fig. 6 (c)).

#### **DESULPHURIZATION STUDIES**

#### SCREENING OF ADSORBENTS

## Evaluation of S sorption capacity of Commercial Activated Carbon Materials (Bare or As received)

**Table 2.** S sorbing ability of different commercial activated carbon materials

S. No.	Sorbent name	*ml-diesel treated/g of adsorbent	S removed (ppm)
1	IG 18	4	134
2	IG 12	4	81
3	IG 8	4	76
4	AC 4	4	12

5	AC 6	4	73
6	AC 12	4	92
7	Calgon carbon as received	4	181
8	Adsorbent carbon	4	229

\* 20 ml initial product collected from the column packed with 5.0 activated carbon and analyzed for S analysis

# EVALUATION OF ADSORPTIVE DESULPHURIZATION POTENTIAL OF ADSORBENT AND CALGON BASED CARBON MATERIALS

**Table 3.** Comparison of the S sorption capacity of Adsorbent carbon as received, adsorbent carbon treated with  $HNO_3$ , adsorbent carbon treated with  $HNO_3$  followed by Ar activation, calgon carbon as received, Calgon carbon treated with  $HNO_3$  followed by Ar activation

Sorbent Amount	5.0 g	10 g	15 g
Sorbent Type	S removed*, (in ppm)		
Adsorbent carbon as received	229	380	410
Adsorbent carbon treated with HNO <sub>3</sub>	105	186	577
Adsorbent carbon treated with HNO <sub>3</sub>	346	518	586
followed by Ar activation			
Calgon carbon as received	181	371	451
Calgon carbon treated with HNO <sub>3</sub>	280	378	488
Calgon carbon treated with HNO <sub>3</sub>	340	399	619
followed by Ar activation			

\* The product under consideration is the first 20 ml diesel obtained through the sorbent bed

\* S content in the diesel feed - 737 ppm

#### STUDIES ON S SORPTION SCALING UP TO 100 g BATCH

Table 4. S adsorption studies on 100 g Adsorbent carbon  $HNO_3$  treated, Ar activated and Calgon carbon as received

S. No.	ml-diesel/g adsorbent	S content in the product (S content removed) (in ppm)	
		Adsorbent carbon activated with HNO <sub>3</sub> followed by Ar activation	Calgon carbon as received
1	0.2	13 (724)	137 (600)
2	0.4	68 (669)	192 (545)
3	0.6	110 (627)	233 (504)
4	0.8	169 (568)	302 (435)
5	1.0	194 (543)	302 (435)
6	1.2	233 (504)	313 (424)
7	1.4	263 (474)	317 (420)
8	1.6	290 (447)	379 (358)
9	1.8	325 (412)	444 (293)
10	2.0	375 (362)	457 (280)
11	2.2	415 (322)	479 (258)
12	2.4	443 (294)	520 (217)
13	2.6	463 (274)	557 (180)
14	2.8	486 (251)	567 (170)
15	3.0	496 (241)	519 (218)
16	3.2	505 (232)	532 (205)
17	3.4	510 (227)	548 (189)

#### **REGENERATION OF ADSORBENT**

 Table 5.
 Comparison of the performance of fresh and regenerated sorbent (100 g Calgon carbon as received)

S. No.	100 g Calgon as received	S content in the product (S removed) in ppm

	ml-diesel/g adsorbent	Fresh sorbent	Regenerated sorbent
1	0.2	137 (600)	97 (640)
2	0.4	192 (545)	110 (627)
3	0.6	233 (504)	162 (575)
4	0.8	302 (435)	256 (481)
5	1.0	302 (435)	297 (440)
6	1.2	313 (424)	370 (367)
7	1.4	317 (420)	387 (350)
8	1.6	379 (358)	443 (294)
9	1.8	444 (293)	505 (232)
10	2.0	457 (280)	512 (225)
11	2.2	479 (258)	548 (189)
12	2.4	520 (217)	549 (188)
13	2.6	557 (180)	551 (186)
14	2.8	567 (170)	554 (183)



#### CONCLUSIONS

#### ACKNOWLEDGMENTS

#### REFERENCES

 B. Viswanathan, P. Indra Neel, T. K. Varadarajan, A Process for the preparation of Activated Carbon from Botanical Sources, Indian Patent File No. 376 CHE 2007

2. V. Gomez-Serrano, M. Acedo-Ramos, A. J. Lopez-Peinado, C. Valenzuela-Calahorrro, Thermochimica Acta, 291 (1997) 109-115

- 3. Joong S. Noh and James A. Schwarz, Carbon 28 (1990) 675
- 4. Mingwang Shao, Debao Wang, Guihua-Yu, Bing Hu, Weichao Yu, Yitai Qian, Carbon 42 (2004) 183-185.

5. J. A. Macia-Agullo, B. C. Moore, D, Cazoria-Amoros, A. Linares-Solana, Microporous Materials 101 (2007) 397-405.

6. Gregg, S. J., Singh, K. S. W., 1982, Adsorption, Surface Area and Porosity, Second ed. Academic Press, London, pp. 195-288.

7. Qingrong Qian, Motoi Machida, Hideki Tatsumoto, Bioresource Technology, 98 (2007) 353-360

8. A. M. Puziy, O. I. Poddubnaya, A. Martinez-Alnso, F. Suarez-Garcia, J. M. D. Tason, Carbon 41 (2003) 1181-1192

9. Thio Christine Chandra, M. M. Mirna, Y. Sudaryanto, S. Ismadji, Chemical Engineering Journal, 127 (2007) 121-129.

10. Chang Yu, Jie Shan Qiu, Yu Feng Sun, Xian Hui Li, Gang Chen, Zong Bin Zhao, Journal of Porous Materials (Article in press)

11. C. Ishizaki and I. Marti, Carbon 19 (1981) 409

12. T. Budinova, E. Ekinci, F. Yardim, A. Grimm, E. Bjornbom, V. Minkova, M. Goranova, Fuel Processing Technology, 87 (2006) 899 – 905

13. M. Madhava Rao, A. Ramesh, G. Purna Chandra Rao, K. Seshaiah, Journal of Hazardous Materials B129 (2006) 123-129

14. A. Macias-Garcia, M. A. Diaz-Diez, E. M. Cuerda-Correa, M. Olivares-Marin, J. Ganan-Gomez, Applied Surface Science, 252 (2006) 5972-5975

15. Ting Yang, Aik Chong Lua, Materials Chemistry and Physics, 100 (2006) 438-444

16. Alaxender M Puziy, Olga Poddubnaya, Amelia Martinez – Alonso, Fabian Suarez-Garcia, Juan M. D. Tascon, Carbon 43 (2005) 2857-2868.