



Low-temperature hydrolysis of carbon disulfide using the Fe–Cu/AC catalyst modified by non-thermal plasma



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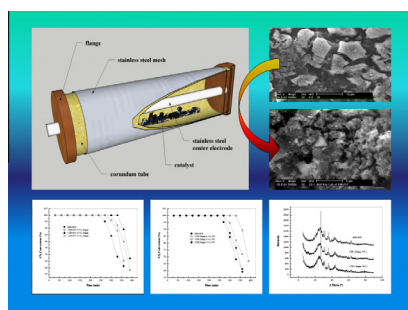
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HIGHLIGHTS

- Catalytic hydrolysis of CS₂ at the low temperature was studied.
- Effect of the modification by non-thermal plasma on catalyst was described.
- Relationship between the activity and properties of catalyst was studied.

GRAPHICAL ABSTRACT

Hydrolysis of carbon disulfide (CS₂) at low temperature over the Fe–Cu/AC catalyst which was modified by non-thermal plasma has been investigated.



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ABSTRACT

The removal of carbon disulfide (CS₂) from gas streams via Fe–Cu/AC catalyst modified by non-thermal plasma (NTP) were investigated. In particular, effects of treatment conditions on the catalyst's properties were studied. The properties change in the catalyst after NTP modification is measured by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscope (SEM). The results showed relatively high capacities of Fe–Cu/AC catalyst modified by NTP for removal of COS. The catalytic activity and sulfur capacity of material enhanced due to the extended oxygen functional groups on the surface of carbons. In addition, the surface area and micro-pore volume on NTP-modified catalysts played another important role in the process of CS₂ removal.

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1. Introduction

Carbon disulfide (CS₂; S=C=S) is released from the burning of fossil fuels, many chemical processes, volcanic eruption, and plant or protein corruption. CS₂ is normally regarded as a significant poison for industrial catalysis and its presence could result in the

deactivation of catalysts and corrosion of reaction equipment [1–3]. Levels of sulfur as low as 1 ppm can effectively poison the activity of a modern bimetallic reforming catalyst. The presence of feedstock CS₂ can also lead to increased corrosion of the reactors used in refinery processes. Furthermore, not only does CS₂ provides economic problems, but also affects the environment. It has been proven to be a major source of acid rain when oxidized to sulfur oxide and to promote photochemical reactions [4,5]. In view of both increasingly stringent environmental regulations and technical requirements for further catalytic processes, deeper

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desulfurization including CS₂ removal from gas streams becomes in high demand.

The hydrolysis of reduced sulfur compounds, including CS₂, was recognized as the most promising process due to the mild reaction condition, cheapness, and higher conversion efficiency. In addition, the final hydrolysis products, CO₂ and H₂S, are much easier to be removed than CS₂ [6–10]. Activated carbon (AC) is an attractive alternative for its low cost, yet it does not show good performance in the deodorization process, because its surface chemistry is not potent enough to enhance the specific adsorption and catalytic processes [11,12]. On the other hand, non-thermal plasma-based techniques for catalyst preparation have recently attracted significant attention for catalyst design and development. It is a fast solvent-free technique and the operative procedure is simple and can be well-controlled. It is also easy to create an ambience for oxidative, reductive, or inactive reactions by changing the feed gas. It can also produce chemically active species on the surface of AC to affect their functions without changing their bulk properties significantly [13–17].

In our previous study, a series of coal-based AC catalysts, combined with metal oxides, were prepared by sol–gel method for CS₂ hydrolysis and their performances for CS₂ hydrolysis were investigated [18,19]. Although these catalyst is an efficient desulfurizer for CS₂ removal, the efficiency still need to further improve. In this paper, NTP treatment technology was introduced to modify the carbon-based catalysts for hydrolysis of CS₂. To improve the hydrolysis activity at low temperatures, we attempt to extent the NTP treatment method for the preparation of Fe–Cu/AC hydrolysis catalyst. The influence of treatment conditions on the physico-chemical properties and catalytic activity was studied.

2. Experimental

2.1. Catalyst preparation and NTP modification

The ash content of fresh AC (LJ-40 commercial) was 12% and specific surface area was 749 m²/g. Firstly, the commercial AC was dipped in a solution of 1 M KOH and boiled for 1.5 h, then washed with distilled water. Secondly, a colloid solution was prepared with a certain amount of metal nitrate solution and a Na₂CO₃ solution. The AC was added to the hydrosol. Thirdly, the sample was treated with ultrasonic for 30 min, dried at 120 °C in the drying oven and calcined at 400 °C for 3 h. Finally the catalyst calcined was dipped in an alkali solution with a certain mass ratio and kept under the ultrasonic for 30 min, then dried for 3 h at 120 °C in the drying oven.

The details of the plasma reactor configuration is described in our previous work [20]. The non-thermal plasma was obtained in a coaxial cylinder-type dielectric barrier discharge reactor by using

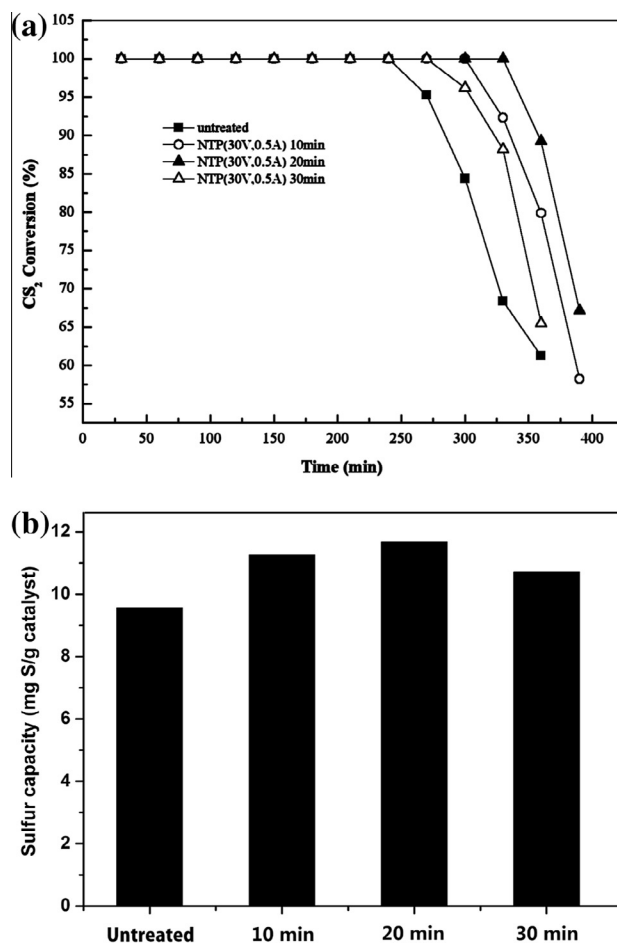


Fig. 2. Hydrolysis conversion activity (a) and sulfur capacity (b) of CS₂ removal on the Fe–Cu/AC catalyst modified by NTP with different time.

a corundum tube (inner diameter 20 mm, outer diameter 25 mm) as a dielectric barrier between the inner high voltage electrode (stainless steel tube, outer diameter 10 mm) and a grounded electrode (stainless steel mesh) on the outer wall (as shown in Fig. 1). The plasma electrical source is produced by Nanjing Su man electron Ltd. and Model is CTP-2000P. A digital oscilloscope (Rigol, DS1052E, 50 MHz/GSa/s) was used for electrical measurements in discharge. The output voltage of plasma generator was measured by a high voltage probe (Pintek, HVP-28HF, 1000:1), and the low voltage probe (LV probe) was used to gather current waveform from the voltage drop across a sampling resistor ($R_0 = 50 \Omega$) connected in series with the ground line of DBD reactor. The plasma

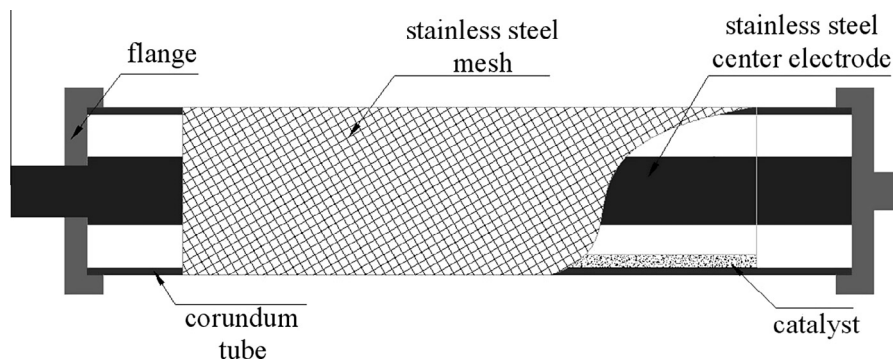


Fig. 1. The configuration of dielectric barrier discharge reactor.

is generated at a discharge input voltage (V) of 10–70 V and a discharge output voltage (kV) of 2.4–6.0 kV. The discharge frequency is 7.8 kHz. All the samples (0.8 g catalyst every time) were placed in the chamber in the same way, and the treatment environment is at atmospheric pressure.

2.2. Characterization

Characterizations of the AC catalysts were carried out as reported elsewhere [18,21], in order to measure the BET surface area and porosity, structure (by X-ray diffraction, XRD), surface chemical content of sulfonic groups (by X-ray photoelectron spectroscopy, XPS).

2.3. Experimental procedure

Desulphurization tests were performed in a fixed-bed quartz reactor under atmospheric pressure [18]. The overall flow rate was controlled using calibrated mass flow controllers. At steady state, a gas N_2 mixture containing $190 \text{ mg/m}^3 \text{ CS}_2$ was introduced into the reactor. In all the tests, the total flow rate was fixed at 100 ml/min , which corresponded to a GHSV (gas hourly space velocity) of 7000 h^{-1} . 0.45 g catalyst was used. Water was introduced using a saturator system. The temperature of the reactor was controlled to 50°C over its entire length by water-bath with circulating pump, with accuracy $\pm 1^\circ\text{C}$.

3. Results and discussion

Figs. 2 and 3 show the activities and breakthrough sulfur capacity (considering breakthrough threshold at $38 \text{ mg/m}^3 \text{ CS}_2$) as a function of the treated time and treated voltage on catalytic hydrolysis of CS_2 , respectively. As shown in Fig. 2(a), the curves of catalytic hydrolysis activity with different treated time: 10, 20, 30 min

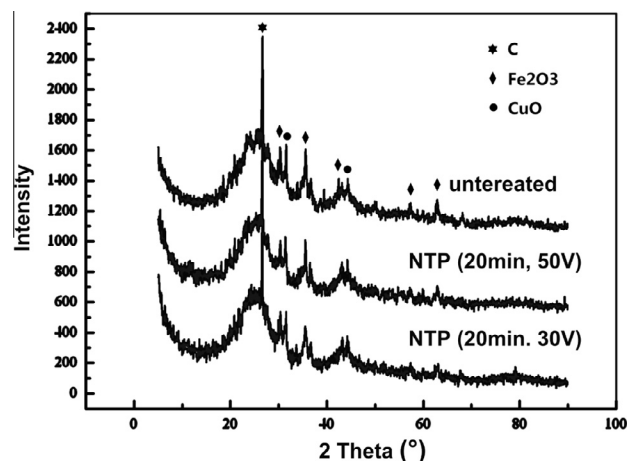


Fig. 4. XRD patterns of catalysts modified by different plasma treatment parameters.

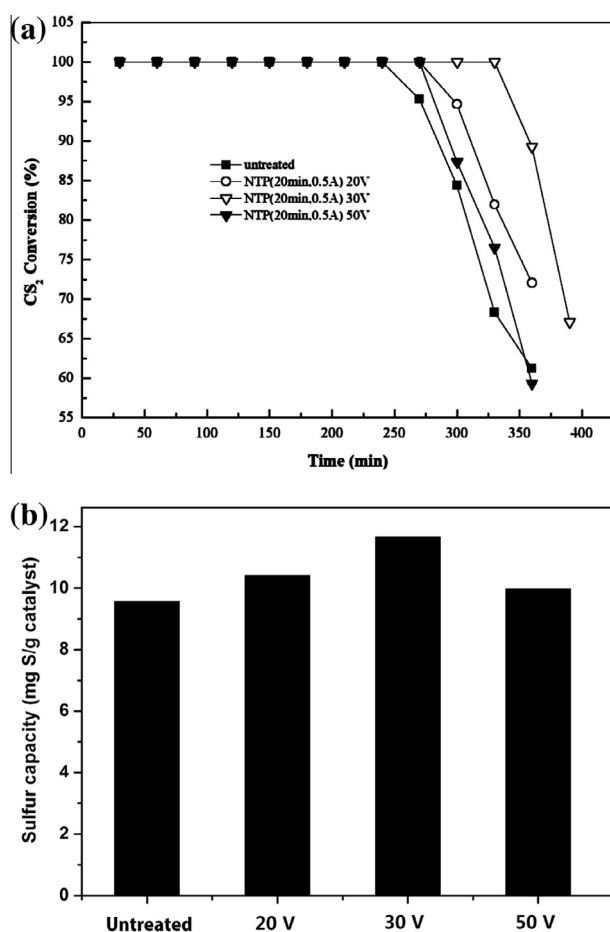


Fig. 3. Hydrolysis conversion activity (a) and sulfur capacity (b) of CS_2 removal on the Fe–Cu/AC catalyst modified by NTP with different voltage.

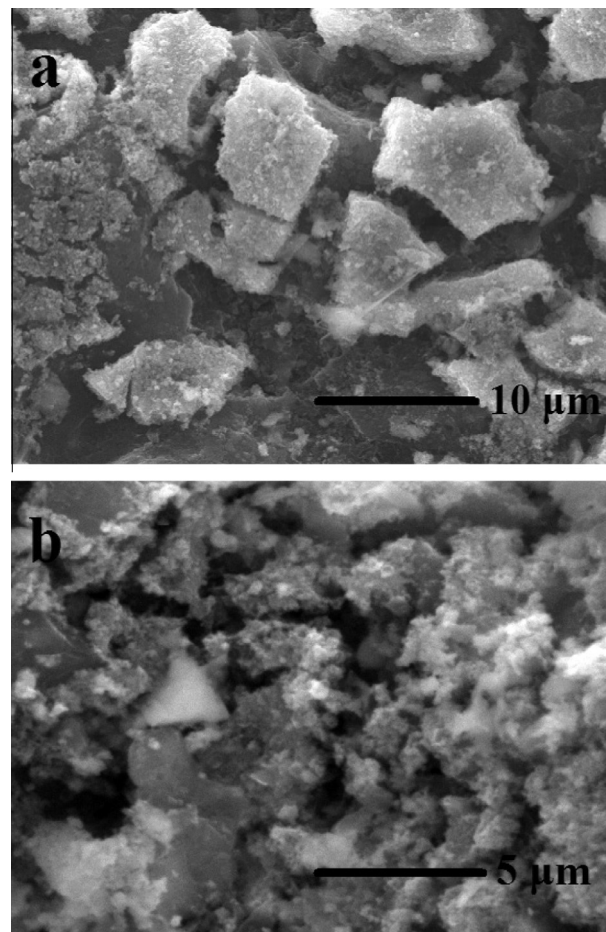
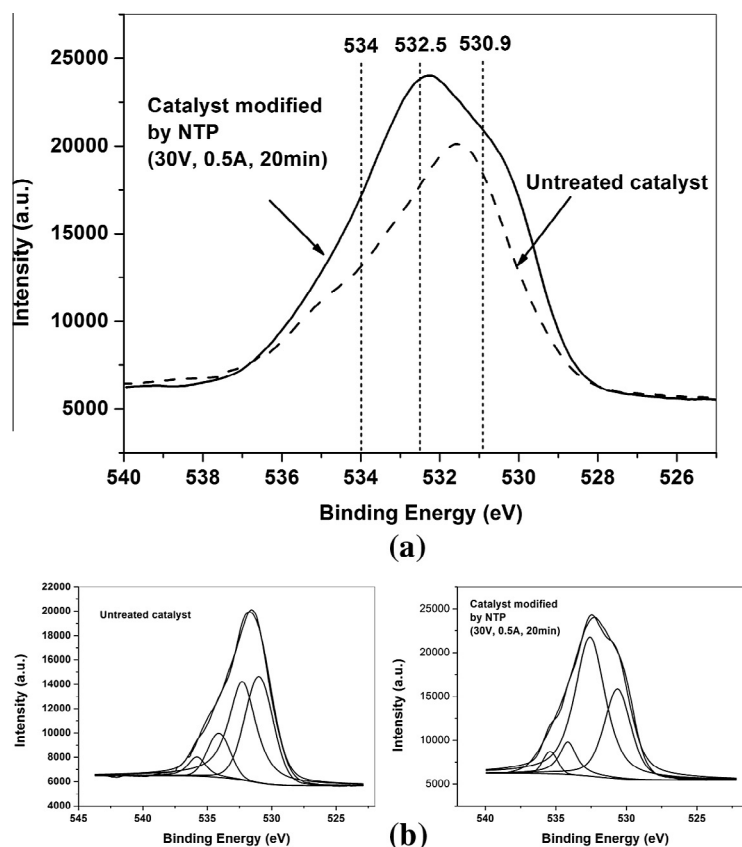


Fig. 5. SEM images of (a) the Fe–Cu/AC catalyst, and (b) the Fe–Cu/AC catalyst modified by NTP.

Table 1

Relative area (%) of O1s XPS for the Fe–Cu/AC catalysts.

	Peak position (eV)	Relative area (%)	Peak position (eV)	Relative area (%)	Peak position (eV)	Relative area (%)	Peak position (eV)	Relative area (%)
Untreated	535.92	5.71	533.98	13.09	532.41	46.75	530.81	34.46
(30 V, 0.5 A) 10 min	535.50	7.32	533.82	7.04	532.55	47.90	531.03	37.75
(30 V, 0.5 A) 20 min	535.59	3.82	533.95	6.38	532.45	52.64	530.84	37.16
(30 V, 0.5 A) 30 min	535.86	5.32	534.07	6.14	532.60	49.49	530.95	39.06
(20 min, 0.5 A) 20 V	536.09	5.39	534.05	10.69	532.51	48.35	530.85	35.57
(20 min, 0.5 A) 50 V	536.26	2.97	534.40	9.05	532.49	53.42	530.83	34.55

**Fig. 6.** (a) XPS spectra (O1s region) of the Fe–Cu/AC catalyst, and the Fe–Cu/AC catalyst modified by NTP; (b) XPS O1s signal of the Fe–Cu/AC catalyst, and the Fe–Cu/AC catalyst modified by NTP fitted by Gaussian functions.

presented similar enhancement of the activity and the removal efficiency initially increased and then decreased with treatment time and the better treatment time was 20 min. In Fig. 3(a) the curves of catalytic hydrolysis activity with different treated input voltage: 20, 30, 50 V also show a similar behavior. The CS₂ conversion of the modified samples was higher than that of the unmodified sample in the whole treated voltage range and when the treated input voltage was 30 V, the catalyst exhibits significantly better performance compared to the other treated input voltage. It seems that both the treated time and input voltage can affect the catalyst's surface properties. To understand the reasons for this phenomenon, the structure and properties of the catalysts were carefully characterized by various methods such as XRD, SEM, N₂ adsorption/desorption and XPS.

Fig. 4 presents the XRD patterns of catalysts treated at different conditions and the untreated sample. The peak intensity of three samples was quite similar and there was little difference in the XRD patterns. This may be because: carbon was noncrystal and

its background peak was obvious. But the amount of metal oxides (Fe₂O₃ and CuO) on the AC surface was far less than AC so that the crystallinity of metal oxides was poor. As shown in Fig. 4, diffraction peaks with strong intensity appeared at $2\theta = 30.175^\circ$, 35.439° , 57.193° and 62.895° , which are matched to the values of Fe₂O₃. The XRD results indicate that NTP treatment did not change the phase of the catalyst.

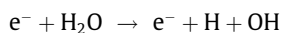
The surface morphologies of the virgin and modified by NTP were observed by SEM. It can be seen that there were some metal oxides into a massive structure uniform coverage the surface of untreated sample (Fig. 5(a)), and it has the metallic luster. Modification with NTP has a visual impact on surface morphology. After NTP, the catalyst's surface become rougher and a considerable amount of deposition with limited depths appeared. Compared with the untreated sample, the active components with small particles rather than a massive structure unevenly covered on the surface of the NTP treated samples. In addition, some active ingredients were deep loaded within the carrier's hole, which

Table 2
Pore characteristics of the catalysts.

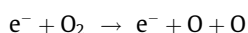
Samples	Surface area/(m ² /g)	Total pore volume/(cm ³ /g)	Average pore radius/(nm)
Untreated	579	0.33	2.33
NTP (30 V, 0.5 A), 10 min	607	0.33	2.18
NTP (30 V, 0.5 A), 20 min	626	0.34	2.15
NTP (30 V, 0.5 A), 30 min	605	0.33	2.18
NTP (20 min, 0.5 A), 20 V	604	0.33	2.18
NTP (20 min, 0.5 A), 50 V	607	0.33	2.18

changed the dispersion of active components. Much smaller particles of the active phase (bright areas in the SEM image) can be observed for the catalysts after NTP treatment.

To analyze the surface characteristics of catalysts in detail, XPS was applied to estimate the amount of O1s. The concentration of O1s on surface of the AC was also detected by XPS and the groups of O binding energy positions were illustrated in Table 1 and Fig. 6. As can be seen from Table 1 and Fig. 6, there were three main functional groups on the catalyst surface, appeared in about 530.90 eV peak was Fe₂O₃ in oxygen, about 532.50 eV peak may appear in the OH[−] oxygen, and about 534.00 eV there was carbon oxygen peak in the oxygen functional groups. A weak peak appeared in about 536.00 eV, it may be the satellite peak. These results fully agree with the description in the literature [22–24]. From the Fig. 6(a), it can be clearly seen that the portions of Fe–O and OH[−] increased as the plasma was treated on the AC. The most probable source of OH radicals produced in the NTP reactor is the high energy electron impact dissociation of water molecules as well as the photo chemical water dissociation resulting from application of the plasma according to the following reactions:



In addition, NTP treatment can produce a large number of oxygen free radicals, which would be adsorbed on the catalyst surface [25,26].



As removal reaction time goes by, CO₂ was detected. This shows that CS₂ has been hydrolyzed. Characterization results of the exhausted catalyst shows that the elemental sulfur, metal sulfide, and sulfate are ultimately generated on the surface of the catalyst. The consumption of basic sites as well as the blocking of pores was considered to be main reason for the deactivation of the catalyst [18,19,21]. We propose the following potential degradation pathways of CS₂: firstly, CS₂ is hydrolyzed to CO₂ and H₂S. In this step, Fe–O, Cu–O, and OH[−] is the active sites for the hydrolysis reaction. Secondly, H₂S is oxidized to sulfate, metal sulfide, and elemental sulfur by oxygen-containing functional groups (Fe–O, Cu–O, and O^{2−}). Therefore, it is easy to understand that higher CS₂ removal efficiency could be obtained using the catalysts which were treated by NTP treatment, which can brought more oxygen-containing functional groups on the catalyst.

The structural parameters of some representative samples treated by the plasma were shown in Table 2. It can be seen that the catalyst specific surface area increased slightly after NTP processing. The result indicated that NTP modification could change the pore structure of the samples. It may be another reason for the catalyst activity increased.

4. Conclusions

In this paper, a series of coal-based active carbon catalysts (Fe–Cu/AC) modified by NTP for CS₂ hydrolysis and their performances for CS₂ hydrolysis at the relatively low temperature of

50 °C were investigated. The catalytic activities results showed that the NTP treated catalysts exhibit better performance compared to the untreated catalyst, and the catalyst displayed the highest activity when the NTP treatment time was 20 min and treated voltage was 30 V. Plasma treatments enhanced the surface area of catalysts and improved the dispersion of catalysts. CS₂, in general, was firstly hydrolyzed to H₂S, which depending on the Fe–O and OH[−] groups. The elemental sulfur, metal sulfide, and sulfate are ultimately generated on the surface of the catalyst. The NTP modification can improve the content of hydroxyl groups and oxygen free radicals on the surface of the catalyst, thus, it can improve the activity of catalyst.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2014.03.021>.

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