



About the process improvement of adsorptive desulphurisation by adding hydrogen donators as additives in liquid fuels

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ABSTRACT

For the use in fuel cell system commercial fuels, like diesel or domestic heating oil, have to be desulphurised to ultra deep sulphur levels of below 1 mg kg^{-1} . To reach this goal the adsorptive desulphurisation using a nickel-based sorbent has been identified. The evaluation of the reaction mechanism reveals in principle the same route as that of the hydrodesulphurisation (HDS) whereas the sulphur is adsorbed by the sorbent instead of being converted to hydrogen sulphide. The required hydrogen for the process is provided out of the fuel itself and not by an external supply of hydrogen. This analysis leads to an easy applicable enhancement of the process by adding a hydrogen donator as an additive to the liquid fuel. In correlation to the mass fraction of the donator the reaction rates and sorbent capacities are improved significantly.

Furthermore the influence of aromatic compounds has been investigated, which exhibit similar molecular structures and chemical properties than comparable high refractory sulphur species. This leads to side reactions especially of di- and tri-aromatics which influence the sulphur adsorption. A shift of the aromatic fraction from mono- to di- and tri-aromatic compounds has been observed as well as the alkylation of di- and tri-aromatics.

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1. Introduction

In order to combine the advantages of fuel cell systems and liquid fuels, like high energy density and long term stability, hydrogen rich syngases are reformed from liquid fuels. The technical implementation of such systems is linked to the introduction of sulphur sensitive catalysts, which are deactivated by the sulphur compounds present in liquid fuels.

As a result of more and more strict directives of the European Union (EU) and EPA (Environmental Protection Agency, USA) the maximum allowed sulphur levels of fuels need to be reduced significantly. These mandatory specifications lower the emission and immission of sulphur dioxide (SO_2) dramatically and enable catalytic exhaust after treatments in mobile applications. An overview of the current sulphur levels and of their development during the last decades is given in Fig. 1. Since the year 2010 almost all fuels with the exception of marine diesel (1000 mg kg^{-1}) and kerosene (3000 mg kg^{-1} , average value below 1000 mg kg^{-1}) must be below 10 mg kg^{-1} (EU) or 15 mg kg^{-1} (EPA) of sulphur. To produce such low sulphur levels the conventional method hydrodesulphurisation (HDS) is employed by refineries at a temperature of $300\text{--}400^\circ\text{C}$ and pressure of 40–50 bar. Sulphur species found in commercial

gasoil after the HDS process include substituted thiophenes, benzothiophenes (BTs) and dibenzothiophenes (DBTs) with one or more alkyl groups [1]. In low-sulphur diesel with $<10 \text{ mg kg}^{-1}$ only highly substituted DBTs are left [2]. It has been reported that alkyl groups in the 4th and 6th positions are refractory to the hydrodesulphurisation process. To reduce the sulphur content of diesel fuel even below $<10 \text{ mg kg}^{-1}$ using current hydrotreating technology, the reactor volume or the catalyst reactivity of the hydrotreating technology has to be three times larger than that currently used [3].

It is not expected that sulphur levels of commercial available fuels will be much lower than the limits defined in the directives.

For fuel cell applications based on liquid hydrocarbons even these sulphur limits are too high for an unrestricted use. The sulphur limits, which may be tolerable for a fuel cell system, are based on the type of catalysts used for the reforming process and for the fuel cell stacks.

A basic distinction can be made between the catalytic reforming processes called steam reforming (SR) [4], autothermal reforming (ATR) [5] and catalytic partial oxidation (CPOX) [6]. As a result of the different operating temperatures, the sulphur tolerances range from about $<1 \text{ ppm}$ for SR, via ATR to CPOX, which shows a tolerance of up to 50 ppm of sulphur for a short time. In [7] it has been shown by equilibrium calculation that reforming fuels of 10 mg kg^{-1} sulphur cause an H_2S -concentration in the syngas of approximately 1 ppm in addition to a COS-concentration of 0.1 ppm. For a fuel cell system that is based on the autothermal reforming and on high

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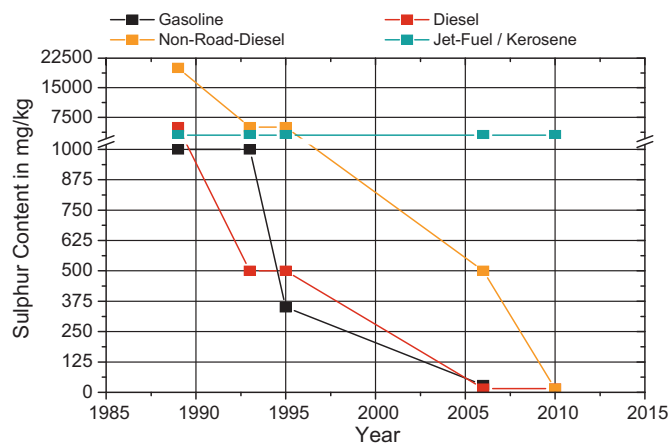


Fig. 1. Sulphur level in liquid fuels related to the directives of the EU and EPA.

temperature fuel cell stacks, like a Solid-Oxide-Fuel-Cell (SOFC), a desulphurisation of fuel below <10 ppm might be sufficient. Hence, a deep desulphurisation <1 ppm is not absolutely necessary for all appliances. However, a desulphurisation down to 0.1–1 ppm leads to H_2S -concentrations of merely 0.01–0.1 ppm. To achieve such low-sulphur contents in fuel a desulphurisation process on-site or on-board must be available. The use of hydrogen, as used in the hydrodesulphurisation (HDS) process, is undesirable due to volume and cost, in particular for mobile systems.

To fulfil the above mentioned requirements different processes are available to desulphurise liquid hydrocarbons without the use of hydrogen. These are in particular oxidation [8,9], extraction [10,11], adsorption [12,13] and biological [14,15] processes. Based on a theoretical validation [16] the adsorptive desulphurisation is considered as the best in terms of costs, simple process design and possible integration especially in mobile FC-system.

2. Adsorption desulphurisation

Currently different sorbent materials are under investigation for a deep desulphurisation of liquid hydrocarbons for the use in fuel cell systems. In the literature the following approaches are specified:

- Zeolites [17–20]
- Activated carbons [21–23]
- Catalysts with carrier material endowed with transition metals like Ni or Cu [24,25]
- Catalysts with noble metals like Pt, Pd, Rh, Au or Ag [26]
- Metal oxides [31].

In particular two main developments are focused for the desulphurisation of middle distillates like diesel and domestic heating oil.

On the one hand the selective adsorption is caused by the so-called Π -complex bonding between the sorbent material and especially polycyclic aromatic sulphur heterocycles (PASH) at ambient temperature. In this process special activated carbons and zeolites are used, which are summarised in Table 1. Depending on the fuel and the sorbent material different selectivities and breakthrough capacities are measured, which amount from $0.5 \text{ mg}_S \text{ g}_{\text{Sorbent}}^{-1}$ up to $10.44 \text{ mg}_S \text{ g}_{\text{Sorbent}}^{-1}$. The most promising sorbent is the zeolite “CDX/Cu(I)-Y” with a breakthrough capacity of $10.44 \text{ mg}_S \text{ g}_{\text{Sorbent}}^{-1}$.

On the other hand nickel based sorbents have been developed, which are used at higher temperatures. The results of different researchers [24–27] are shown in Table 2. It can be seen that

temperatures of 200–220 °C are necessary to reach an ultra deep desulphurisation and sufficient capacity. The best capacity has been reached with a $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$ sorbent of $7.1 \text{ mg}_S \text{ g}_{\text{Sorbent}}^{-1}$ at 220 °C.

A partial vaporization of a JP-8 fuel, by which the high boiling fractions and complex sulphur species are removed, leads to an improved capacity of the used sorbent to $12.8 \text{ mg}_S \text{ g}_{\text{Sorbent}}^{-1}$.

In Kim et al. [23] different sorbent materials like activated carbon, aluminium oxides (Al_2O_3) and $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$ have been investigated in terms of reaction mechanism. Instead of commercial diesel a model fuel consisting of 0.43 % w/w sulphur compounds (dibenzothiophene, 4,6-dimethyldibenzothiophene), 0.27% w/w nitrogen compounds (quinoline, indoline), 10.21% w/w aromatic compounds (benzene, naphthalene) and 88.09% w/w paraffine (n-decane, n-hexadecane, n-tetradecane) has been used. It has been demonstrated that all sorbent materials remove along the sulphur species even the aromatic and nitrogen compounds. The selectivity and capacity increase in the order of polycyclic aromatic compounds (PAC) < sulphur compounds < nitrogen compounds. The activated carbon shows the highest capacity for sulphur species followed by the nickel-based sorbent and finally the aluminium oxide.

As the reaction mechanism of the nickel-based material a direct interaction of the sulphur with the active side of the adsorbent is supposed, because sterical hindrances of alkylated methyl- or ethyl groups like 4,6-dimethyldibenzothiophene (4,6-DMDBT) constrain the adsorption.

The activated aluminium oxide shows an adsorption affinity proportional to the electrochemical negativity of the adsorbent. Hence electrostatical interactions are involved in the reaction mechanism.

The affinity of the activated carbon was not correlated to defined properties, like the electrochemical potential. It is supposed instead that hydrogen bonds may play an important role [23].

The companies Mesoscopic Devices [28], TDA Research [29] and Aspen Product Groups have developed different systems for the adsorptive desulphurisation. The used non-specified sorbents can be regenerated with air at 500 °C for 1–2 h [28] or at 400 °C for 2–4 h [29]. Degradation of the adsorption performance by the regeneration has not been observed.

The sorbent of “TDA SulfaTrap™-D1” [29] reaches a capacity of $4.8 \text{ mg}_S \text{ g}_{\text{Sorbent}}^{-1}$ at a breakthrough criterion of 10 mg kg^{-1} by the desulphurisation of a commercial JP-5 with 500 mg kg^{-1} of sulphur. The breakthrough capacity in [28,30] is not specified indeed.

3. Reactive adsorption

The reactive adsorption is a combined hydrodesulphurisation and adsorption process. At the process of the reactive adsorption metal catalyst such as nickel (Ni) on aluminium oxide (Al_2O_3) or metal oxides is used in the presence of hydrogen. The metal catalyst reacts with the sulphur to form metal sulphides and fixes the sulphur on the surface by chemisorption. At this reaction only the sulphur atom gets adsorbed on the surface whereas the hydrocarbon molecule which is saturated by hydrogen is left in the fuel. This effect is demonstrated in Fig. 2. The reactive adsorption is a new process, which has already reached an industrial stage and is used at the patented S-Zorb-Process of ConocoPhillips [31] and at the RTI-Trend process of the Research-Triangle-Institute (RTI) [31,32]. These processes are illustrated in Fig. 3(A) and (B). Compared to the conventional HDS at the S-Zorb process for diesel and gasoline the hydrogen sulphide H_2S is not returned to the product stream. At the S-Zorb process the sulphur atom is adsorbed on the surface of the catalyst, so that recombination reactions of hydrogen sulphide H_2S and olefins to mercaptanes as well as the hydrogenation of aromatics are avoided.

Table 1
Breakthrough capacity at 1 mg kg⁻¹ of sulphur using Π -complex forming sorbents at ambient temperature [20].

Sorbent	Fuel	Breakthrough capacity at 1 kg _{fuel} ⁻¹
HCeYIE-2	Model JP-8	2.3
Activated carbon (Calgon Typ PCB)	U.S. diesel	<0.5
CDX/Cu(I)-Y (VPIE)	U.S. diesel	10.44
	JP-5/kerosene	<0.5
CDX/Ni(II)-Y (SSIE)	U.S. diesel	6.11
Cu(I)-Y (VPIE)	U.S. diesel	8.89
Ni(II)-Y (SSIE)	U.S. diesel	5.06
Selexsorb CDX	U.S. diesel	2.63
PdCl ₂ /AC	JP-5/kerosene	1.9

Table 2
Breakthrough capacity at 10 mg kg⁻¹ of nickel-based sorbents [24,25].

Sorbent	Fuel	Sulphur content (mg kg ⁻¹)	Temperature (°C)	Breakthrough capacity (mg _s g ⁻¹)
Ni/SiO ₂ -Al ₂ O ₃	Gasoline	305	20	<0.8
Ni/SiO ₂ -Al ₂ O ₃	Gasoline	305	200	7.6
Ni/SiO ₂ -Al ₂ O ₃	JP-8	736	220	7.1
Ni/SiO ₂ -Al ₂ O ₃	Light JP-8	380	220	12.8
KYNiE-3	Light JP-8	380	80	4.44
KYNiE-3	Light JP-8	380	80	1.48

For this reason the desulphurization to below 10 mg kg⁻¹ is less complex and the costs can be reduced. At the S-Zorb-process demonstrated in Fig. 3(A) is actuated an entrained-bed reactor (1) by process pressures of 7–35 bar and process temperatures of 400–473 °C. Thereto the distillate gets converted with hydrogen in the gas phase and initiated in the entrained-bed reactor. After the adsorption of the sulphur in the two-phase reactor (gas–solid), the loaded catalyst is initiated in the regenerator (2) by a continuous circulation. At the two-phase reactor the sulphur gets oxidised and subsequent reduced with hydrogen. By this regeneration cycle sulphur dioxide SO₂ is generated and the catalyst can be used without reduction of degree of efficiency for four to five years [31]. An essential advantage of the process of the reactive adsorption is that the properties of the product such as density, distillation range, cetane number, colour, and cloud-point do not change. By the RTI-process (Transport Reactor for Naphtha Desulphurisation) are used metal oxides instead of metal catalyst by process temperatures of 425–535 °C. The hydrogen which is used in the process is mainly required to avoid thermal cracking reactions and to saturate the desulphurised hydrocarbon molecules. At the two-phase reactor illustrated in Fig. 3(B) the sulphur gets adsorbed from the hydrocarbon bonding and subsequently the adsorbent is continuously put in the regenerator. The oxidation of metal sulphides to metal oxides delivers hydrogen sulphides SO₂. In the Claus-process for example the hydrogen sulphides SO₂ can be transformed into elementary sulphur. Another reduction of the adsorbents is compared with the S-Zorb-process not required. Thus the adsorbents can directly be introduced to the desulphurisation step. By the analysis and by the reactions on the analysis it was asserted that selective all sulphur bondings are removed independent of the structure and complexity.

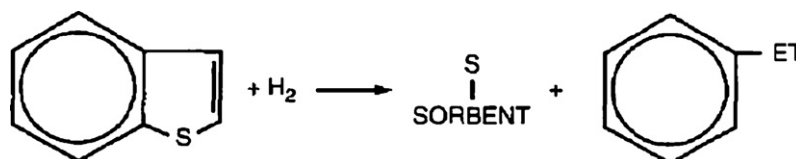
Thereby it is possible to reduce the sulphur content of gasoline and diesel below 10 mg kg⁻¹. The patented UTC-Fuel-Cell process of Cocolicchio et al. in [33], which is particularly developed for fuel cell applications, also used nickel based adsorbents. The hydrogen H₂ is already brought to dissolution before entering the desulphurization reactor, consequently a two-phase reactor (fluid–solid) is actuated. The hydrogen can be introduced in the process as absolute hydrogen in the form of a technical gas or as a recirculated synthesis gas.

In the following the experimental set-up for the investigations of the adsorptive desulphurisation using nickel based sorbents will be described. After the verification of the reaction mechanism the reaction kinetic and optimum operation conditions will be presented. This leads to the process enhancement by adding hydrogen donators to liquid fuels. Finally the influence of aromatic compounds on the adsorptive desulphurisation and vice versa will be discussed due to the similar physical and chemical properties in comparison to the existent refractory sulphur species.

4. Experimental set-up

The set-up of the test bench for the experimental examination of several commercial sorbents is shown in Fig. 4. The set-up has been designed to investigate the reaction kinetic, the chemical equilibrium in relation to the relevant parameters and to activate various sorbents.

As seen in the process scheme the reactor for desulphurisation denoted by (1) exhibits a fixed bed volume of 0.1–0.3 dm³. It is heated radial by a high temperature heater. The necessary gases, like air, nitrogen or hydrogen, are dosed by mass-flow-controllers (2) and conditioned by a pre-heater (3) for drying or activation

**Fig. 2.** Reaction mechanism of reactive adsorption [31].

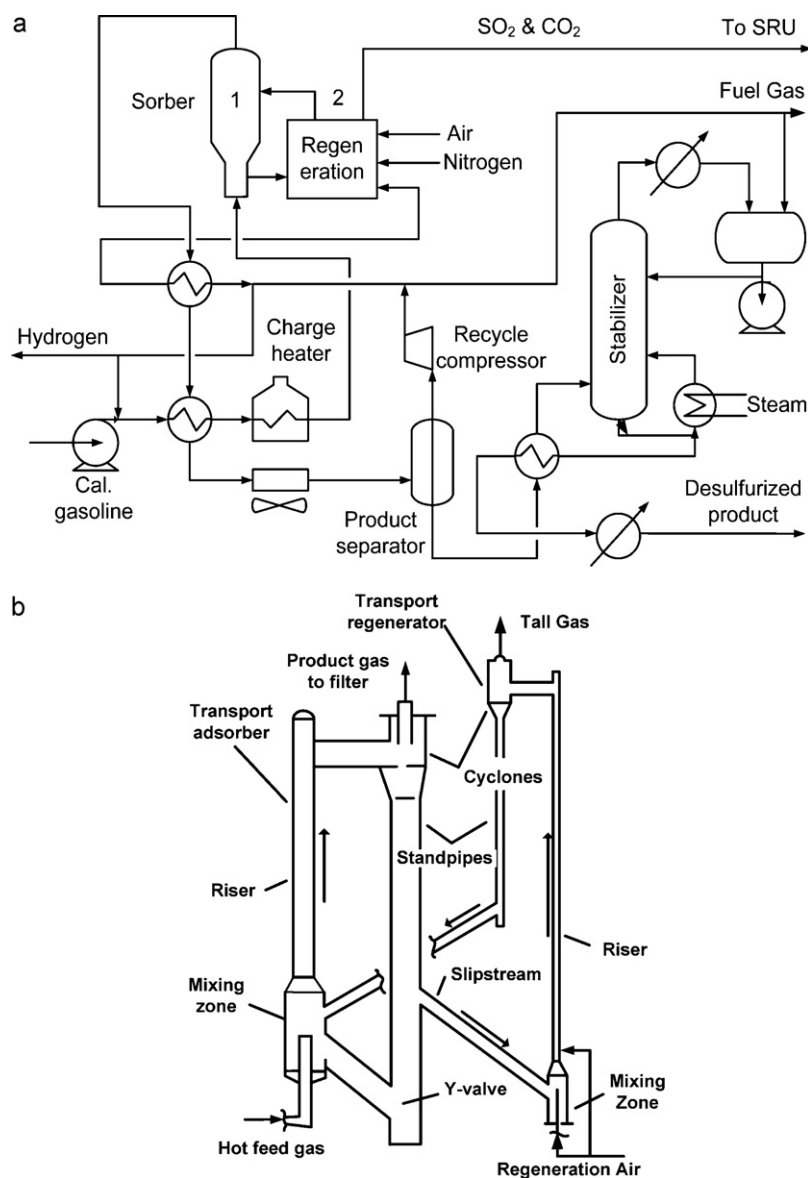


Fig. 3. S-Zorb-process of ConocoPhillips (A) and RTI-Trend-process of Research-Triangle-Institute (B) [31].

of the sorbent. Related to the used sorbent different activation procedures, which differ in the gas composition, temperature characteristic and holding time, are to be applied.

By the high temperature valve (4) the gas supply can be switched off and the fuel can be fed by a micro-controller-pump (5). At the outlet of the reactor (1) the pressure can be adjusted up to $p = 10$ bar manually by a pressure valve (6). Further an electrically activated valve (7) ensures a controlled sampling of the desulfurised fuel. The analysis method to determine the sulphur level and the sulphur species has been described in [7,34].

Three different commercial fuels have been used for the investigation as well as pure aliphatic fuel (Shellsol D) and pure monoaromatic fuel (Shellsol A). The properties of the fuels are summarised in Table 3.

To identify the best sorbent for ultra deep desulphurisation different activated carbons, molecular sieves and nickel-based sorbents have been tested by van Rheinberg et al. [7]. Activated carbon and molecular sieves performed a desulphurisation of Fuel 2 of approximately 50% down to 20 mg kg^{-1} as the best. Moreover nickel based sorbents have been identified to be sufficient ones, which reach sulphur level of $<1 \text{ mg kg}^{-1}$ in all investigated

petroleum based commercial liquid fuels like diesel or domestic heating oil. The best nickel-based sorbent investigated is the one of Südchemie, called FCDS-LQ3, with whom the present study has been conducted.

5. Reaction mechanism of nickel based sorbents

In van Rheinberg et al. [7] it has been shown that there is a strong correlation between the breakthrough of sulphur by the adsorptive desulphurisation and the molecular structure and number of substituents of the sulphur species itself. A closer inspection revealed that the breakthrough of the following sulphur species is detected in the order indicated here:

- 1,4,6-/1,4,8-Trimethyl-dibenzothiophene (TMDBT) or 2,4,6-TMDBT.
- 4,6-Dimethyl-dibenzothiophene (DMDBT) and 4-ethyl (E),6-MDBT.
- 2,6-/3,6-DMDBT and 1,3-/1,4-DMDBT.

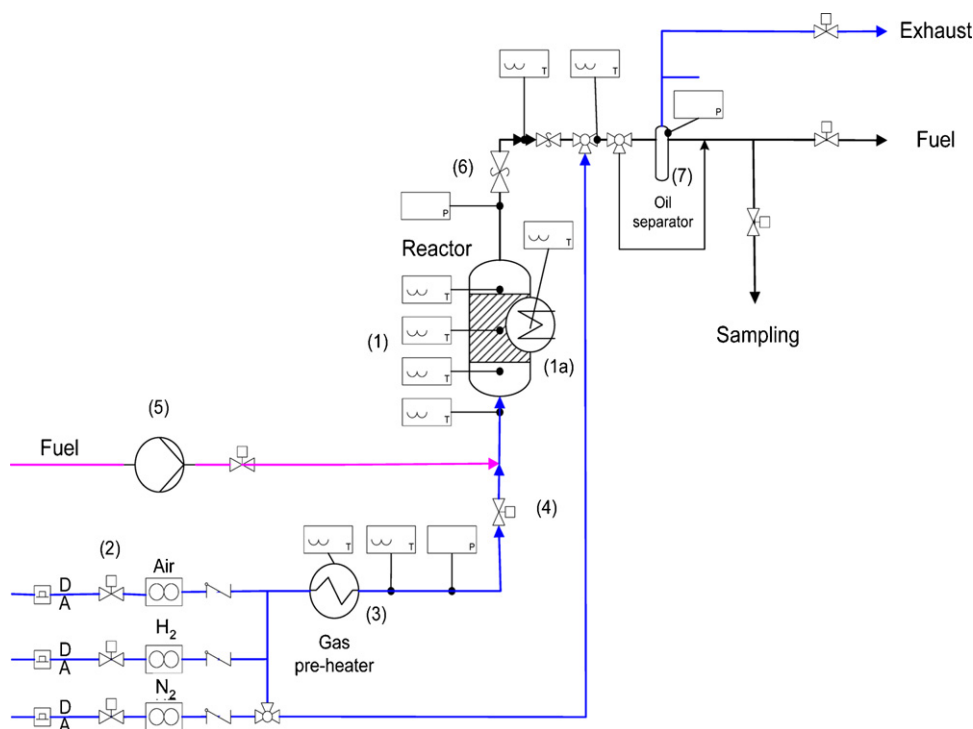


Fig. 4. Experimental set-up for analysing several sorbents for the adsorptive desulphurisation of liquid fuels.

Table 3

Properties of commercial liquid fuels used for the present investigation.

Parameter	Value	Fuel 1	Fuel 2	Fuel 3	Shellsol A	Shellsol D
Density	kg m ⁻³	849.6	826.1	847.5	871	795
Dyn. viscosity	cSt (20 °C)	4.58	4.239	4.48	n.a.	n.a.
Heating value	MJ kg ⁻¹	42.43	43.1	42.8	n.a.	n.a.
Paraffine	% w/w	n.a.	n.a.	n.a.	<1	60
Naphthene	% w/w	n.a.	n.a.	n.a.	<1	40
Aromatic content	% w/w	n.a.	2.5	n.a.	>99	<200 ppm
Monoaromatic compounds	% w/w	n.a.	16.1	n.a.	>99	n.a.
Diaromatic compounds	% w/w	n.a.	2.2	n.a.	n.a.	n.a.
Triaromatic compounds	% w/w	n.a.	0.3	n.a.	n.a.	n.a.
Sulphur content	mg kg ⁻¹	850	50	537	<0.5	<2
Cloud point	°C	-8	-9	n.a.	n.a.	n.a.
Cold filter plugging point	°C	n.a.	-9	n.a.	n.a.	n.a.

- 4-Methyl-dibenzothiophene (MDBT), 4-ethyl-dibenzothiophene (EDBT), 1-MDBT, and 2/3-MDBT.
- Dibenzothiophene (DBT).

The earliest breakthrough is shown by DBTs with three (TMDBT) and then with two (DMDBT) alkyl groups, occupying both the 4th and 6th positions as shown in Fig. 5. Followed by species with two alkyl groups, with only one group located in the 4th position, are recorded. Subsequently all DBTs with one alkyl group, independent of the position, and finally DBT itself are detected. An analysis of the benzothiophenes (BT) during the same experiment reveals a similar trend and the following BTs are successively detected:

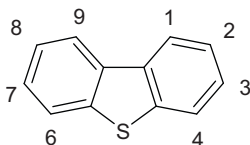
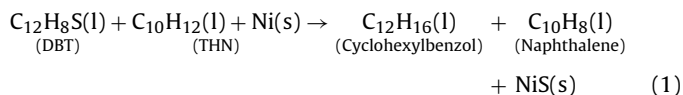


Fig. 5. Molecule structure of dibenzothiophene (DBT).

- C₃-trimethyl-benzothiophene (TMBT) at $t = 13.13$ min retention time, position of alkyl groups not identified.
- 2,3,5-TMBT and TMBTs, position of alkyl groups not identified.
- 2,3-Dimethyl-benzothiophene (DMBT).
- 2,4-, 2,5-/4,7-/3,7-, 2,4-DMBT.

The selectivity of the nickel based sorbent, which depends strongly on the molecule structure of the sulphur species, indicates that the sulphur atom itself interacts with the active sides of the sorbent. To verify the reaction mechanism the desulphurisation of a model fuel was performed. The diaromatic compound 1,2,3,4-tetrahydronaphthalene (THN) was endowed with 2000 mg kg⁻¹ of dibenzothiophene. Using gas chromatography–mass spectrometry (GC–MS) the species cyclohexylbenzol and naphthalene have been identified additionally after the desulphurisation process. The molecule structure and reaction are illustrated in Fig. 6. Hence the reaction of adsorptive desulphurisation of the model fuel using nickel based sorbents can be defined as:



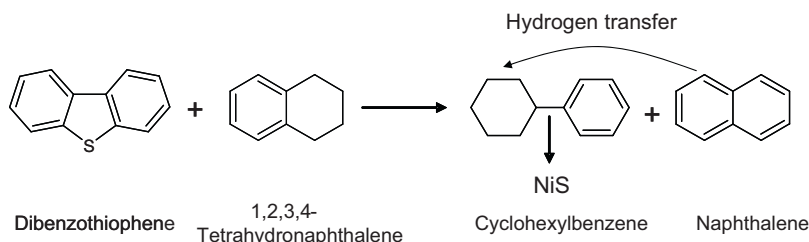


Fig. 6. Reaction mechanism of nickel based sorbent.

Thus the reaction of dibenzothiophene, tetrahydronaphthalene and the active nickel on the sorbent surface to the products cyclohexylbenzol, naphthalene and nickelsulphide is taking place. Along the adsorption of the sulphur atom an internal hydrogen transfer from tetrahydronaphthalene to cyclohexylbenzol becomes apparent. Hence not only an adsorption of sulphur atom takes place as expected. Astonishingly the reaction mechanism of adsorption desulphurisation is similar to those of the reactive adsorption of the S-Zorb process [31] or hydrodesulphurisation (HDS) [35] as described above. The main difference is the fuel internal provision of hydrogen in comparison to an external supply, by which the gaseous hydrogen is solubilised in the fuel at high pressures and temperatures. Hence the confirmed reaction mechanism can be described as an internal hydrodesulphurisation and a parallel selective adsorption of the sulphur on the catalyst (sorbent) surface by the formation of nickelsulphides. Along the irreversible adsorption of sulphur species, reactions and transformations of other educts are catalysed. Consequently the adsorption desulphurisation is as well a continuous and selective poisoning of the nickel-based material, acting as a sacrificial catalyst for the fuel cell system.

To analyse the optimum operation conditions a study of the adsorption process using the nickel-based-sorbent has been performed as described in [7]. By this evaluation it was found that the desulphurisation of liquid fuel is independent of the system pressure. An effect on the process could not be verified due to the incompressibility of the fuel medium. If the process is running at higher temperatures within the boiling range, the fuel has to be pressurised correspondingly to avoid unintentional evaporation.

If the main reaction mechanism of sulphur adsorption via nickel based sorbents is now examined like a hydrodesulphurisation process, the desulphurisation of high and low sulphur fuel is reduced to a reaction rate of 1st and 2nd order respectively. This assumption is feasible as long as the sorbent is not saturated and one mass-transfer-zone is still available in minimum. For this purpose a modified residence time is calculated according to Eq. (2):

$$\tau = \frac{m_{\text{Ads}}}{\dot{V}_{\text{liquid}}(T)} = \frac{m_{\text{Ads}}}{\dot{V}_{\text{liquid}}(15^\circ\text{C})} \cdot \left(1 - a \cdot \frac{(\vartheta - 15^\circ\text{C})}{\rho(15^\circ\text{C})}\right)^{-1} \quad [\text{g h cm}^{-3}] \quad (2)$$

m_{ads} [g] is the mass of the sorbent, $\dot{V}_{\text{liquid}}(T)$ [$\text{cm}^3 \text{h}^{-1}$] the volume flow of the liquid fuel, a [$\text{m}^3 (\text{kg K})^{-1}$] the factor of thermal expansion of the fuel and $\rho(15^\circ\text{C})$ [kg m^{-3}] the density of the fuel. Based on this analysis factor, the reaction kinetic of 1st order is defined by:

$$r_{\text{Ads}} = k_{\text{Ads}} \cdot c_s \quad (3)$$

r_{Ads} [$\text{cm}^3 (\text{g h})^{-1}$] is the reaction velocity of the adsorptive desulphurisation, k_{Ads} [$\text{cm}^3 (\text{g h } c_s)^{-1}$] the rate constant and c_s [mg kg^{-1}] the sulphur concentration of the fuel.

After rewriting this equation to a rate of change of c_s and integrating the first order time behaviour is found:

$$\ln(c_s) = \ln(c_{s,0}) - k_m \cdot T \quad (4)$$

The reaction rate of 2nd order is written as:

$$r_{\text{Ads}} = k_{\text{Ads}} \cdot c_s^2 \quad (5)$$

Then the second order time behaviour leads to:

$$\frac{1}{c_s} = \frac{1}{c_{s,0}} + k_m \cdot T \quad (6)$$

In Fig. 7 it can be seen that the desulphurisation of low sulphur Fuel 1 with 50 mg kg^{-1} of sulphur follows a reaction rate of 2nd order according Eq. (6). The removal of sulphur over Ni/NiO-sorbent is strongly temperature dependent. At a temperature of 200°C and modified residence time of $\tau > 0.001 \text{ g h cm}^{-3}$ a desulphurisation below 1 mg kg^{-1} is achieved. The rate constant is increasing with the reaction temperature from 100°C to 200°C . At lower temperatures the sulphur level cannot be reduced to ultra low contents only by increasing the residence time. Even a residence time of about 2 h at 100°C does not lead to a significant reduction of sulphur.

A higher temperature of above 200°C leads to a decrease of the rate constant again, so that the optimum reaction temperature has been determined at $200\text{--}210^\circ\text{C}$. The lowest sulphur level of $< 0.2 \text{ mg kg}^{-1}$ of Fuel 1 was reached at a temperature of 200°C and residence time of 0.83 h. In this case the exact sulphur level could not be measured at all because it was below the detection limit of 200 ppb of the analyser.

For high sulphur fuels (Fuel 2) the reaction rate follows a 1st order as shown in Fig. 8 as well as for low sulphur fuels the rate constant is increasing with reaction temperature. A similar reduction of reaction rates as observed for low sulphur fuels (Fuel 1) at temperature of 230°C could not be verified. The differences in the order of reaction are caused by the absolute sulphur content in consideration of the fraction of high substituted DBT. The desulphurisation of high sulphur fuels is of 1st order due to the high fraction of simple removable sulphur species. Hence the sulphur

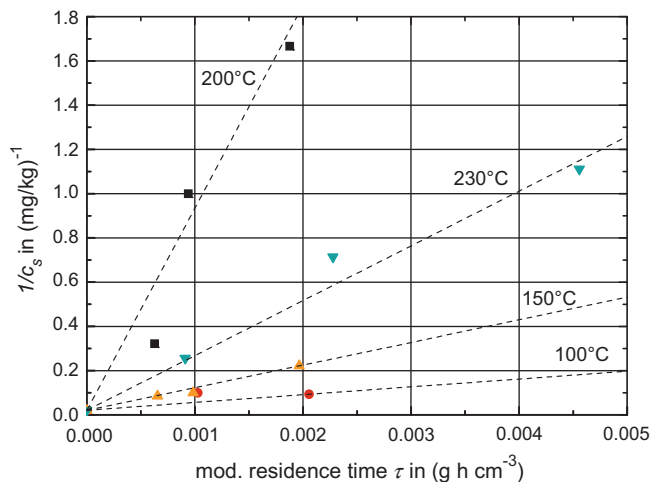


Fig. 7. Dependency of temperature and modified residence time on the reciprocal sulphur content of low sulphur fuels (Fuel 1).

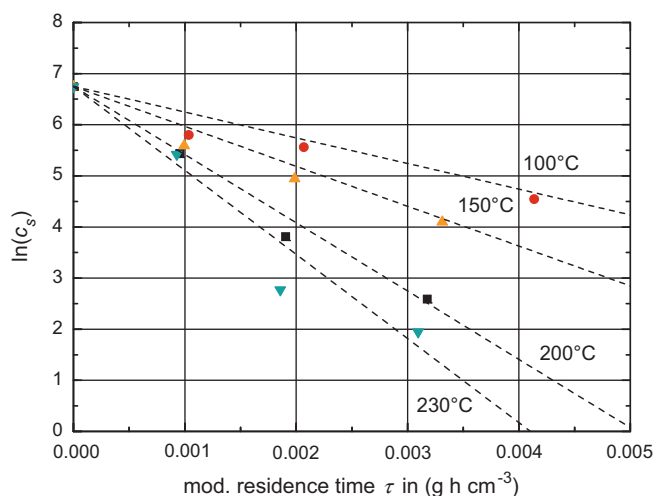


Fig. 8. Dependency of temperature and modified residence time on the reciprocal sulphur content of high sulphur fuels.

level is decreasing immediately and only a small fraction of high substituted and difficult removable sulphur species are left. Low sulphur fuels consist of a significant fraction of high resistant sulphur species, so that long residence times are necessary to reach ultra low sulphur levels.

In consideration of the formal kinetic order the rate constants of the overall desulphurisation reaction can be determined for Fuel 1 and Fuel 2 by using the Arrhenius diagram of Fig. 9. The values of activation energy E_A and rate constant $k_{m,i}$ are summarised in Table 4. The activation energy of the sulphur Fuel 1 of 72.9 kJ mol^{-1} is higher than that of high sulphur Fuel 2, caused by the greater fraction of high substituted DBT and BT with sterical hindrances. Following this argument the rate constant of the desulphurisation of Fuel 2 is higher as for Fuel 1.

To verify whether the internal hydrogen transfer or the adsorption of sulphur affects the reaction rate predominantly, 5% w/w of tetrahydronaphthalene has been added to Fuel 2. The diaromatic compound is oversaturated by four hydrogen atoms, can be dehydrogenated simply and acts as a hydrogen donor. At $\tau = 0.0019 \text{ g h cm}^{-3}$ mod. residence time (LHSV = 0.5 h^{-1}) the sulphur is removed from 850 mg kg^{-1} down to 14 mg kg^{-1} instead of 45 mg kg^{-1} and at $0.001 \text{ g h cm}^{-3}$ to 23 mg kg^{-1} instead of 229 mg kg^{-1} respectively. This improvement demonstrates the great impact of

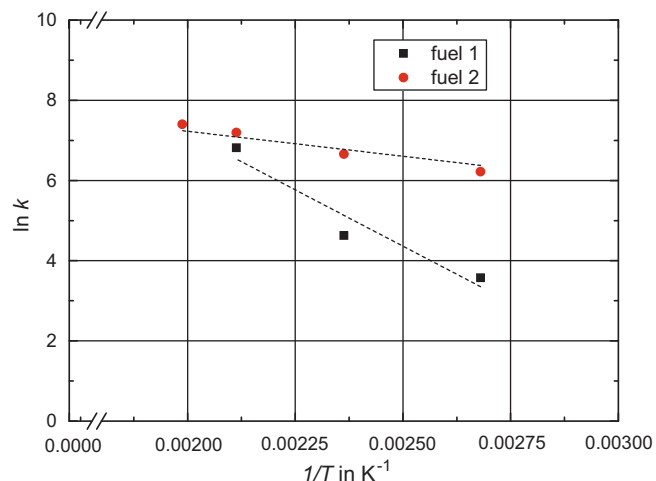


Fig. 9. Arrhenius diagram of rate constants for high and low sulphur fuels.

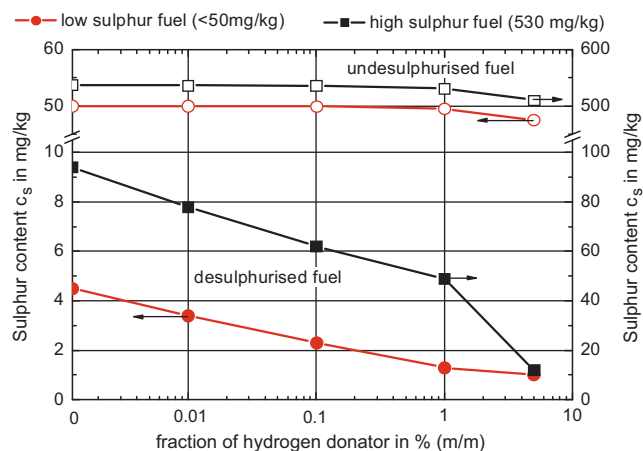


Fig. 10. Improvement of adsorptive desulphurisation by adding hydrogen donors as additives in liquid fuels. ($\vartheta = 200^\circ \text{C}$, $p = 5 \text{ bar}$, LHSV = 1 h^{-1}).

the internal hydrogen transfer on the reaction rates impressively.

Hence, significant improvements in the reaction rate of the adsorptive desulphurisation can be performed not only by optimisation of the sorbent itself, but also by modification of the liquid fuel. This has been verified by similar investigation with Fuel 2 and Fuel 3 of Fig. 10. A higher fraction of the used hydrogen donor leads to lower sulphur levels. For high sulphur fuels (Fuel 3) the addition of 5% w/w of the hydrogen donor leads to the most significant improvement of the reaction rate. By this addition a desulphurisation of 97.8% from 510 mg kg^{-1} to 11 mg kg^{-1} sulphur is achieved. The dilution effect is negligible as shown in Fig. 6 additionally.

For low sulphur fuels the addition of hydrogen donor and desulphurisation feature a logarithmical interrelationship. A drastic reduction at 5% w/w of hydrogen donor similar to high sulphur fuels is not monitored. This is reasonable, because the high sulphur content requires a corresponding amount of hydrogen, which is offered by the over dosage of the donor. In comparison to the desulphurisation of low sulphur fuels the direct interaction of the atom with the sorbent surface is the rate determining step. Hence an excess of dissociated hydrogen leads only to a moderate improvement of the reaction rate.

Moreover the capacity of the sorbent is improved by adding hydrogen donor to liquid fuels. In Fig. 11 the breakthrough curves of Fuel 1 (50 mg kg^{-1} sulphur) with and without 5% w/w of a hydrogen donor are compared.

Desulphurising the unadditivated low sulphur fuel yields a linear breakthrough curve starting at below 1 mg kg^{-1} of sulphur and reaching 5 mg kg^{-1} after $300 \text{ l fuel l}^{-1}$ sorbent. In comparison using the additivated fuel a high performance of the desulphurisation down to 1 mg kg^{-1} of sulphur can be achieved until $600 \text{ l fuel l}^{-1}$ sorbent. Due to the progression of the breakthrough curve using hydrogen donors it gets obvious that if a critical activity of the sorbent is achieved the sulphur concentration increases significantly and approaches the original curve. Hence the provision of hydrogen enables a removal of even high residual sulphur species at lower activities of the sorbent. If the activity for the deep desulphurisation falls below the critical value, the sulphur level is rising immediately. A capacity enhancement with a factor of 1.2–2.6 is recorded assuming a breakthrough criterion of 10 mg kg^{-1} or 5 mg kg^{-1} sulphur respectively.

For high sulphur fuels the additivation of 1% w/w or 5% w/w hydrogen donor leads to a capacity improvement of 36% and 46% respectively.

Table 4
Activation energy E_a and rate constant k_m .

Fuel	Reaction	E_a (kJ mol ⁻¹)	$k_{m, 100^\circ C}$ (cm ³ (g h c _s) ⁻¹)	$k_{m, 200^\circ C}$ (cm ³ (g h c _s) ⁻¹)
1	2nd order	72.9	35.738	502
2	1st order	13.8	915.15	1334

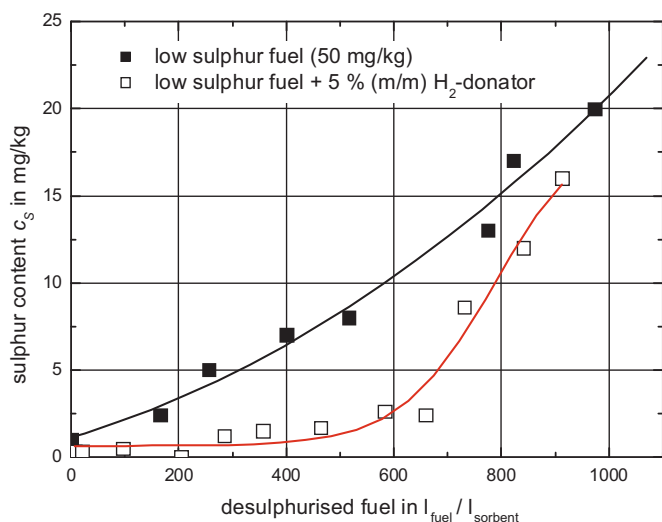


Fig. 11. Improvement of capacity using low sulphur Fuel 2 without performance additives ($\vartheta = 200^\circ\text{C}$, $p = 5$ bar, LHSV = 1 h⁻¹).

In the literature it is reported that an improvement of the adsorptive desulphurisation based on nickel sorbents is achieved by the addition of alkanols, like methanol, ethanol or water [36]. The improvement is only present at lower fractions of alkanols. Higher fractions of alkanols lead to an adverse effect. For example an addition of 0.5% w/w of methanol yields the best performance whereas when using a fraction of 1% w/w no significant improvement of the capacity is reached.

In contrast the fraction of the used hydrogen donator in this paper correlates directly with the reaction kinetic and sorbent capacity. Especially capable hydrogen donators are oversaturated hydrocarbons, which can easily be dehydrogenated and feature non-polar properties contrary to the compounds used by Clemons et al. [36]. For a future application in fuel cell system the addition of the additive can be performed already in refineries or at another logistic location. This can even result in a metering unit

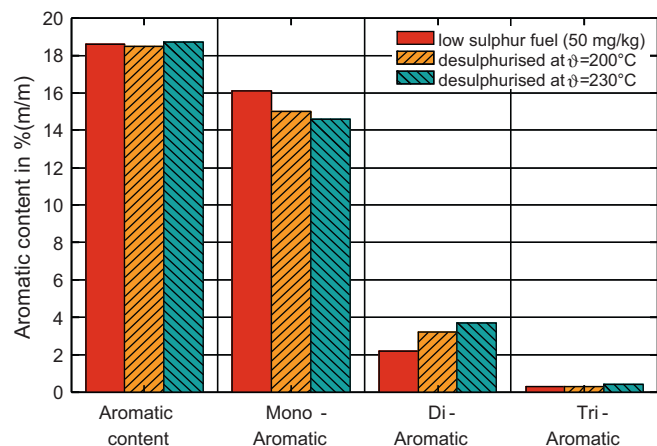


Fig. 12. Distribution of aromatics after the adsorptive desulphurisation subjected to the reaction temperature.

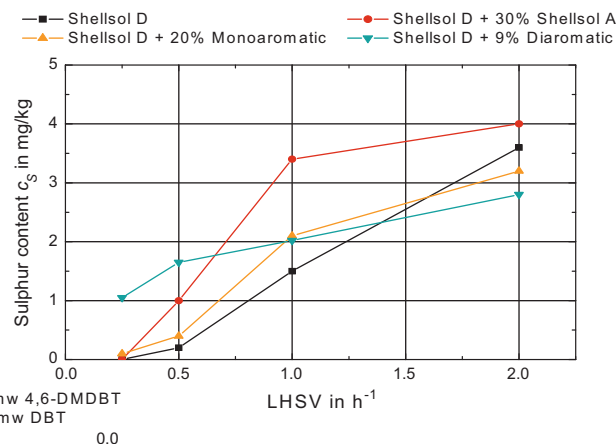


Fig. 13. Impact of aromatic content on the adsorptive desulphurisation (sulphur species: 5 mg kg⁻¹ 4,6-DMDBT, 15 mg kg⁻¹ DBT at $\vartheta = 200^\circ\text{C}$, $p = 5$ bar).

in the fuel cell systems itself, having a separate storage tank like add-blue applications in vehicles for exhaust after treatments.

Due to the detected hydrogen transfer during adsorptive desulphurisation using nickel-based sorbents it has to be clarified, which side reactions occur and how the hydrogen is provided out of the fuel. Therefore the aromatic compounds have been investigated due to their similar chemical and physical properties compared to refractory sulphur species.

6. Aromatic compounds

In Fig. 12 the aromatic hydrocarbons of Fuel 1 according to EN 12916 untreated and desulphurised via adsorption desulphurisation are shown. As a function of reaction temperature a decreasing of monoaromatic and an increasing of di- and triaromatic compounds become evidence. The overall aromatic content is kept constant. Such a shift of the aromatic fractions has been observed

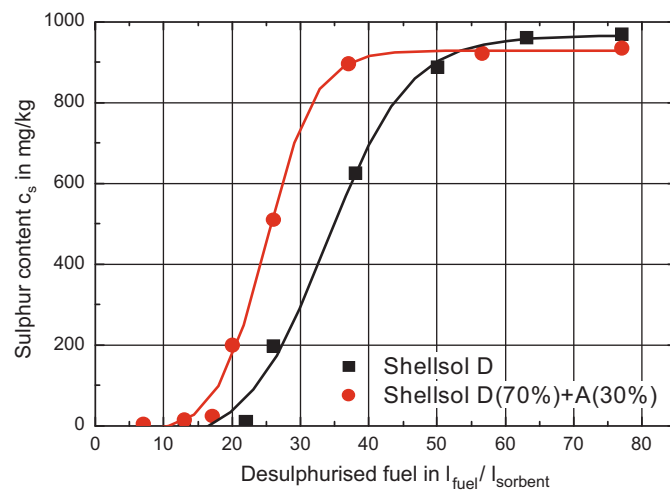


Fig. 14. Impact of aromatic content on the breakthrough curve and capacity of nickel-based sorbent (500 mg kg⁻¹ BT, 500 mg kg⁻¹ DBT, $\vartheta = 200^\circ\text{C}$, $p = 5$ bar, LHSV = 0.5 h⁻¹).

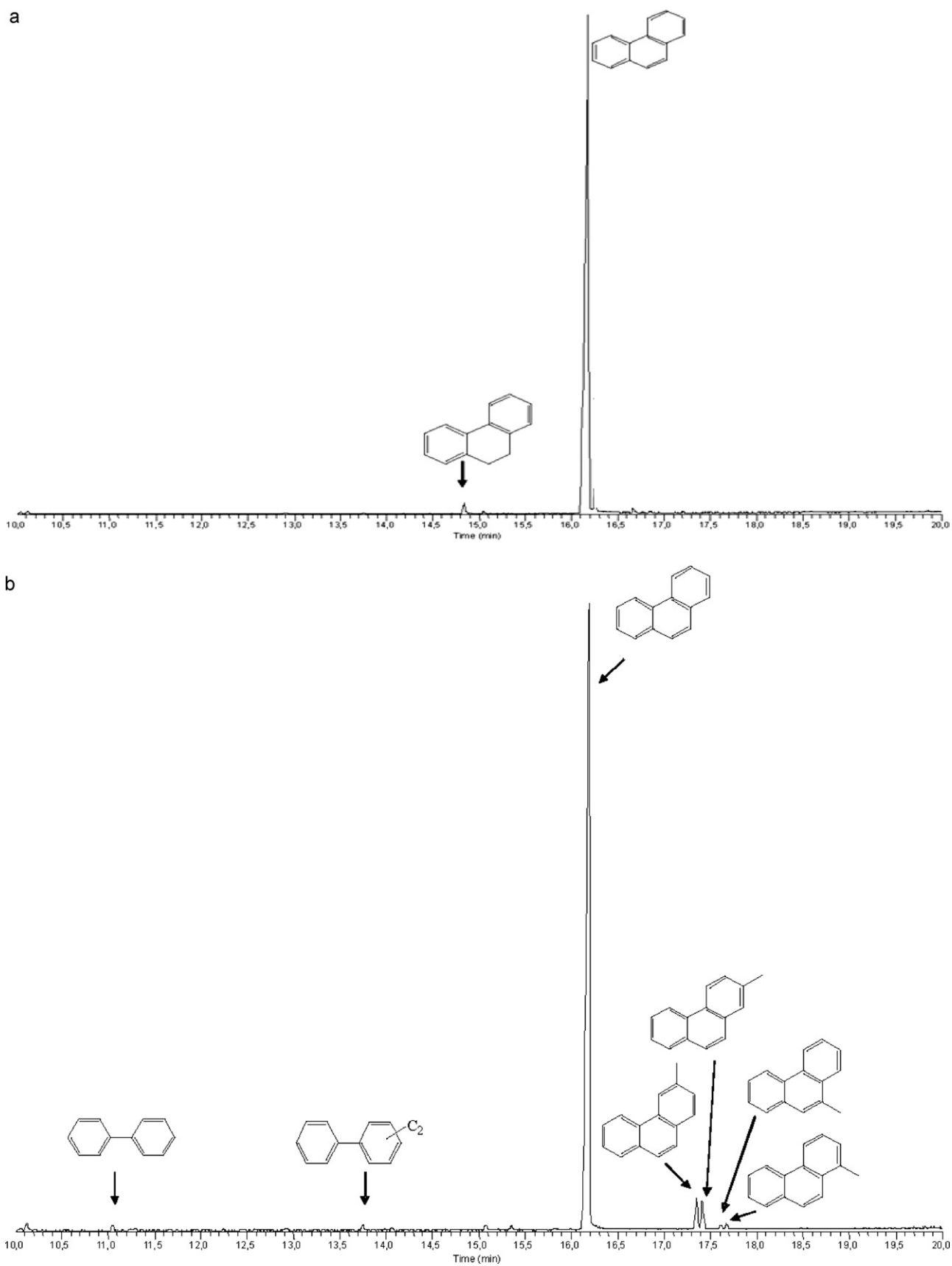


Fig. 15. GC–MS chromatogram (A) before and (B) after the adsorptive desulphurisation of Shellsol D +5% w/w triaromatic compounds endowed with 5 mg kg^{-1} 4,6-DMDBT, 15 mg kg^{-1} DBT.

by all used low sulphur fuels. It can be seen that at 230 °C the side reactions gain to a 1.5 % w/w reduction of monoaromatic compounds and in return a increasing of di- and triaromatic compounds of 1.5% w/w and 0.1% w/w for Fuel 1 respectively. Due to the similar molecule structure and chemical properties of polycyclic aromatic hydrocarbons (PAHs) to polycyclic aromatic sulphur heterocycle (PASHs) reactions are evoked in all fractions of aromatic compounds.

To point out the effect of adsorptive desulphurisation on the aromatic content and vice versa, investigations with following model fuels have been performed:

Model Fuel 1: Shellsol D (pure aliphatic fuel)

Model Fuel 2: Shellsol D + 30% Shellsol A (pure monoaromatic fuel)

Model Fuel 3: Shellsol D + 20% monoaromatic compound (o-xylol)

Model Fuel 4: Shellsol D + 9% diaromatic compound (naphthalene)

Model Fuel 5: Shellsol D + 5% triaromatic compound (phenanthrene)

The model fuels have been endowed with 15 mg kg⁻¹ DBT and 5 mg kg⁻¹ 4,6-DMDBT and are desulphurised at 200 °C and 5 bar. Gorek [37] has analysed the aromatic content and distribution in commercial domestic heating oil (DHO) and found a monoaromatic content of 20–32% w/w, diaromatic compounds of 2.8–7.5% w/w and triaromatic compounds of 0.36–3.3% w/w. Fröhling [38] looked on the quality of diesel fuel in Germany in the same manner and found an average content of monoaromatic compounds of 23% w/w, diaromatic compounds of 4% w/w and triaromatic compounds of 0.6% w/w. Hence, the chosen mixture represents the maximum to be due aromatic fraction according to Gorek [37].

The results of the model fuel desulphurisation are presented in Fig. 13 and reveal that the admixture of 20% monoaromatic compounds has no negative effect on the reaction kinetic of adsorptive desulphurisation. In comparison to the aliphatic fuel (Model Fuel 1) the sulphur contents, dependent on the liquid hourly space velocity (LHSV) or residence time, are equal within the accuracy of measurement, because the differences between the various fuels are rather small and are even smaller than the error estimate of the experimental set-up.

By adding 30% w/w Shellsol A the desulphurisation becomes influenced at flow rate of LHSV > 0.5 h⁻¹. Due to the composition of Shellsol A, containing mainly C₃-substituted monoaromatic compounds, this test run is comparable to the admixture of 20% monoaromatics. But it can be seen that 30% w/w of Shellsol A causes higher sulphur levels for LHSV > 0.5 h⁻¹ in comparison to 20% w/w of monoaromatics. This would even result in a lower sorbent capacity.

The mixture with 9% w/w diaromatics causes sulphur levels above 1 mg kg⁻¹ at LHSV < 1 h⁻¹ which means a slight degradation of the adsorption process in comparison to the desulphurisation of aromatic free Model Fuel 1. Due to the similar molecular structure and chemical properties of naphthalene to DBT or 4,6-DMDBT it leads to unintentional side reactions, which influence the reaction kinetic and equilibrium negatively.

To quantify the effect of aromatics on the sorbent capacity a breakthrough curve of the sulphur has been recorded with the same admixture as used in Model Fuel 2 endowed with 500 mg kg⁻¹ BT and 500 mg kg⁻¹ DBT. From Fig. 14 the breakthrough of sulphur appears earlier by the presence of 30% w/w of monoaromatics resulting in a lower capacity of 13.4 g_s l_{sor}⁻¹ than 17 g_s l_{sor}⁻¹.

To get a deeper understanding of the subsiding processes among the sulphur adsorption itself, GC-MS analysis of the original and desulphurised model fuels are performed.

For example the analysis of the admixture Shellsol D + 20 % w/w monoaromatics (Model Fuel 3) reveals a diaromatic fraction of 0.1% w/w in the original and 1% w/w in the desulphurised fuel.

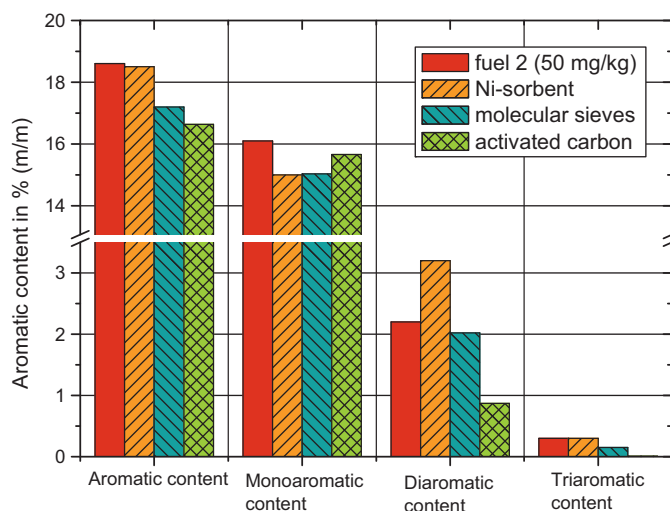


Fig. 16. Impact of adsorptive desulphurisation of molecular sieves and activated carbons on the aromatic content of commercial fuels in comparison to nickel based sorbents.

Unfortunately a classification of the appeared diaromatics was not possible caused by the high peak of the monoaromatic compound in the chromatogram at retention times of 5–9 min. The admixture of Shellsol D + 5% w/w triaromatics (Model Fuel 5) leads to a triaromatic content of approx. 8.5% w/w in the desulphurised fuel. A classification of the triaromatics produced by the adsorptive desulphurisation succeeded as shown in Fig. 15(A) and (B).

In the GC-MS chromatogram of the original fuel (A) phenanthrene can be identified easily. An additional signal is detected by the compound 9,1-dihydrophenanthrene. In the GC-MS chromatogram of the desulphurised fuel, shown in Fig. 15(B), distinct signals of methylated species of the phenanthrene become apparent along the phenanthrene. Moreover biphenyl and alkylated biphenyl are detected, which originates by the hydrogenation of 4,6-DMDBT and DBT. Similar changes were analysed by the addition of 9% w/w naphthalene. Along naphthalene methyltetralene, methyl-naphthalene and dimethylnaphthalene were identified precisely.

Due to the detection of substituted aromatic compounds (di- and triaromatics) the adsorptive desulphurisation leads to a catalyst induced fragmentation of aliphatic hydrocarbons, whose radical fragments bond as methyl groups at the aromatic structure by electrophile aromatic substitution reaction. Additionally an aromatisation is aroused by an acid and de-/hydrogenation component of the bifunctional catalyst [39]. By this reaction hydrogen is released, which is used for the desulphurisation or hydrogenation respectively.

The presence of aromatic compounds influences the adsorptive desulphurisation by nickel based sorbents considerably less than the adsorption by activated carbon or molecular sieves. Different types of these sorbent materials have been tested for the desulphurisation of commercial liquid fuels as reported in [7]. The performed results are rather small because the low selectivity to polycyclic aromatic sulphur heterocycles (PASHs) is the main reason. In Fig. 16 the aromatic content of the original fuel is compared to the ones of the desulphurised fuel by using the same type of activated carbon, which has been presented in Kim et al. [23], and commercial molecular sieves. For both sorbents, especially the di- and triaromatic fractions are removed about several percentages. Due to the fact that commercial liquid fuels like diesel or domestic heating oil will always feature a di- and triaromatic fraction, these types of sorbents are insufficient to reach ultra deep sulphur levels for the in situ desulphurisation in fuel cell systems.

7. Conclusion

The determination of the optimum operating conditions demonstrates that the adsorptive desulphurisation via nickel-based sorbents is independent of the system pressure but strongly influenced by the reaction temperature and residence time. The optimal operation conditions of 200 °C and 5 bar lead to ultra deep sulphur levels of <1 mg kg⁻¹ for commercial liquid fuels, like diesel and domestic heating oil. A suitable system pressure is only necessary to avoid a phase change of the liquid fuel only in the case the reaction temperature is close to the boiling temperature.

For the evaluation of additional influencing parameter the reaction mechanism of the nickel-based sorbent has been identified. In the case of the adsorption desulphurisation the same mechanism as for the hydrodesulphurisation (HDS) is taking place. Thereby the well known direct route of HDS proceeds combined with an adsorption of the sulphur atom. The main difference identified is the supply of hydrogen. During adsorption an internal provision of hydrogen is provoked in comparison to an external supply during HDS, by which the gaseous hydrogen is solubilised in the fuel at high pressures and temperatures. Hence the proposed reaction mechanism can be described as an internal hydrodesulphurisation by selective adsorption of sulphur through the formation of nickel-sulphides. Along the irreversible adsorption of sulphur species, reactions and transformations of other educts are catalysed. Consequently the adsorption desulphurisation is as well a continuous and selective poisoning of the nickel-based material, acting as a sacrificial catalyst for the fuel cell system.

This knowledge leads to the approach to improve the adsorptive desulphurisation not by an optimisation of the sorbent but of the liquid fuel. The outcome of this is an addition of hydrogen donors which offer hydrogen in the liquid phase for the adsorption and parallel proceeding hydrogenation. The addition affects the reaction kinetic, leads to lower sulphur concentration and higher capacity of the sorbent. The improvement correlates directly to the mass fraction of the hydrogen donor. Especially appropriate donors are oversaturated liquid hydrocarbons, which can simply be dehydrogenated and feature non-polar properties.

The selectivity of the sorbent depends on the molecule structure of the sulphur species, because of the direct interaction of the sulphur atom with the active elements on the sorbent surface. Benzothiophene and dibenzothiophene with sterical hindrance are most refractory, as especially DBT with alkylation on 4th and 6th positions. In consideration of the number of alkylated groups (trimethyl-, dimethyl-, methyl-DBT) including 4th and 6th positions are breaking through successively. Thereon molecules with substitution only at the 4th position, substitution on an unspecified position and finally the basis structure DBT are detected. Not only the selectivity but also the capacity of the sorbent turned out to be lower for complex sulphur species, dependent on the number and location of substitution.

Aromatic hydrocarbons are forcing side reactions due to their likewise molecule structure in comparison the polycyclic aromatic sulphur heterocycles (PASHs). Thus the aromatic content influences the adsorption process and vice versa. The presence of di- and triaromatics causes a degradation of equilibrium and capacity of the sorbent. A quantitative shift of the aromatic distribution from monoaromatics to di- and triaromatics was observed.

Hence the bifunctional sorbent or catalyst leads to an aromatisation, which release hydrogen for the desulphurisation process.

In spite of this, the influences of aromatics on the adsorptive desulphurisation via nickel-based sorbents are less than by using

activated carbon or molecular sieves. Among this the much better selectivity and capacity confirms the use of nickel-based sorbent to desulphurise commercial liquid fuels, especially middle distillates as diesel or domestic heating oil, to ultra low sulphur levels of <0.2 mg kg⁻¹.

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