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Desulfurization of Jet Fuel for Fuel Cell-based APU Systems in Aircraft

Y. Wang, J. Pasel, R. Peters, D. Stolten, Forschungszentrum Jülich GmbH, Jülich, Germany

Summary

To prevent the catalysts in fuel cell systems from poisoning by sulfur containing substances the fuel to be used must be desulfurized to a maximum of 10 ppmw of sulfur. Since the conventional hydrodesulfurization process employed in the refinery industry is not suitable for mobile fuel cell applications (e.g. auxiliary power units, APUs), the present study aims at developing an alternative process and determining its technical feasibility. A large number of processes were assessed with respect to their application in fuel cell APUs. The results revealed that a two-step process combining pervaporation and adsorption is a suitable process for the on-board desulfurization of jet fuel. The investigations to evaluate this process are presented in this paper. Seven different membrane materials and ten sorbent materials were screened to choose the most suitable candidates. Further laboratory experiments were conducted to optimize the operating conditions and to collect data for a pilot plant design. Different jet fuel qualities with up to 1650 ppmw of sulfur can be desulfurized to a level of 10 ppmw.

1 Introduction

Fuel cells are well suited for on-board power supply in aircraft, ships and heavy duty vehicles. The use of fuel cell systems in aircraft offers the possibility to simplify the aircraft layout. Important systems in aircraft, i.e. the gas turbine powered auxiliary power unit (APU) for electricity supply, the fuel tank inerting system and the water tank, can be substituted by one single system, the fuel cell system. The waste heat of the fuel cell system can be used for ice protection. These measures reduce the consumption of jet fuel, increase aircraft efficiency and allow operation with low emissions. Additionally, the costs for aircraft related investments, for aircraft maintenance and operation can be reduced. APUs driven by conventional gas turbines operate at an efficiency of about 15% on the ground [1], while an APU based on autothermal reforming of diesel or gasoline in combination with a Polymer Electrolyte Fuel Cell (PEFC) can achieve a system efficiency of up to 36–37% [2, 3].

To operate fuel cells with the fuel available on board, the fuel is converted into a hydrogen-rich gas by a process of catalytic reforming. Since both the catalysts in the reformer and in the fuel cell can be deactivated by the sulfur compounds contained in the fuel, the liquid fuel must be desulfurized to a level with a maximum of 10 ppmw (parts per million by weight) of sulfur [4, 5, 6]. Whereas diesel fuel for road vehicles within the EU is already desulfurized at the refinery, jet fuel is permitted to have up to 3000 ppmw of sulfur worldwide [7, 8]. An analysis of fuel samples showed that jet fuel with a total sulfur content ranging from 300 ppmw to 700 ppmw has been marketed in Europe. On-board desulfurization is therefore required for the use of fuel cell auxiliary power units (APUs) in aircraft.

2 Process Design

In the petroleum industry, low-sulfur fuels are often obtained by hydrocracking processes or hydrotreating processes, so-called hydrodesulfurization (HDS). However, this conventional method is highly inconvenient for reducing sulfur compounds to the desired level in a mobile fuel cell system with a capacity range of 5-10 kW, since improvements of the hydrodesulfurization efficiency are limited by increasingly severe operating conditions and escalating costs [9, 10].

Therefore a newly developed desulfurization process is needed for this application. To this end, a large number of processes described in the literature were assessed with respect to their application in fuel cell APUs. A very promising approach combining a pervaporation and adsorption process is presented in this paper. The simplified process flow is shown schematically in Figure 1.

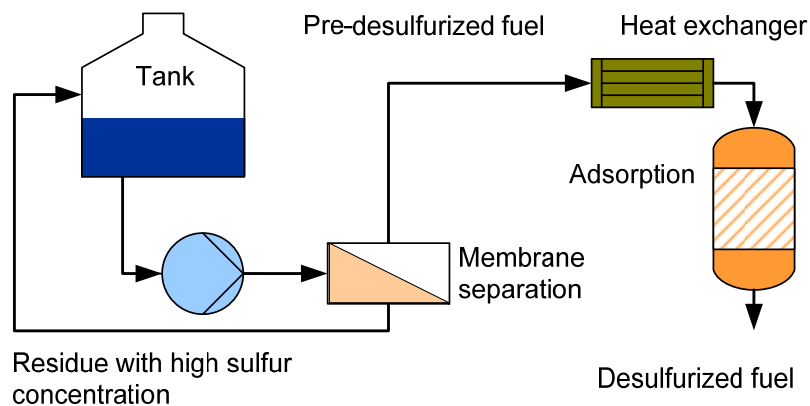


Figure 1: Process flow sheet of combined pervaporation and adsorptive desulfurization.

In this approach, the liquid fuel is first heated to the desired temperature and then fed into the membrane section in which the pervaporation is applied to reduce the sulfur content to relatively low levels. Subsequently, the pre-desulfurized liquid fuel is further treated by an integrated fixed-bed adsorption, while the residue with enriched sulfur content is channeled back to the aircraft's fuel tank.

Desulfurization by pervaporation is a process that extracts aromatics from aliphatic hydrocarbons by solvent diffusion transport through a non-porous membrane. Partial vaporization occurs as a result of vacuum, while the membrane acts as a sulfur-selective barrier between the two phases: the liquid phase retentate and the vapor phase permeate. The sulfur molecules can be pulled through the membrane and concentrated at the permeate stream if aromatics preferentially diffuse through the polymer. The other concept is to use a membrane which enriches the sulfur content in the retentate side by the opposite effect [11, 12, 13].

Desulfurization by adsorption is a technology which uses a solid adsorbent to selectively adsorb organosulfur compounds from refinery fuel streams. Adsorptive desulfurization only employs physical adsorption in which organosulfur compounds stay on the solid sorbent

surface in the original form. Regeneration of the sorbent is done by flushing the spent adsorbent with a desorbent resulting in a highly concentrated organosulfur compound flow. The adsorption process is performed under mild conditions and no H₂ is consumed. It is anticipated that sulfur can be removed to the ultraclean level of 10 ppmw or even lower [9, 10].

3 Pervaporation Experiments

The pervaporation experiments were conducted on a lab scale. In the present study, the permeation flux J_p is calculated by weighting the permeate relative to the outer surface of the membrane. The separation factor is determined as $\beta = (C_s)_{Per} / (C_s)_{Feed}$. It denotes the ratio between the weight fraction of sulfur components recovered in the permeate and the weight fraction of sulfur components entering the process. The measured separation factors along with the corresponding permeate flux for six different membranes are shown in Figure 2.

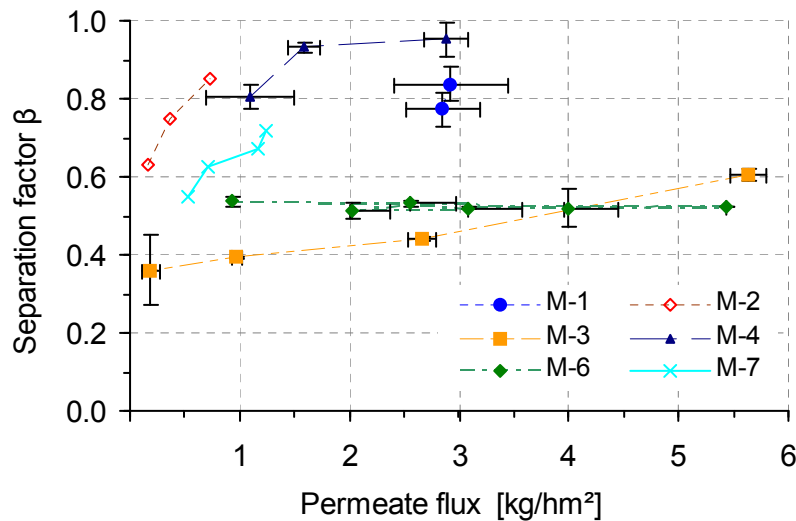


Figure 2: Membrane screening using Jet A-1 with 564 ppmw S for M-1, M-2 and M-3; Jet A-1 with 712 ppmw S for M-4, M-6 and M-7 with operating conditions as: feed temperature T_{feed} : 70 – 140 °C, feed flow rate \dot{V}_{feed} : 300 – 720 ml/min, permeate temperature T_{per} : -196 °C, and permeate pressure p_{per} : 1 – 50 mbar (results with 95% confidence intervals).

The best pervaporation behavior is obtained with the polyurethane membrane M-3 for treating Jet A-1 with 564 ppmw S. Depending on the operating conditions, a separation factor from 0.40 to 0.60 can be achieved with a corresponding permeate flux of 1.00 kg h⁻¹ m⁻² to 5.64 kg h⁻¹ m⁻². However, the pervaporation performance with membrane M-3 was unstable and a drastic degradation effect was even observed after a certain experimental period. Additionally, membrane M-6 is also considered to be a promising candidate. The separation factor amounts to approximately 0.52 with permeate fluxes of 0.93 – 5.40 kg h⁻¹ m⁻² for treating Jet A-1 with 712 ppmw S. Therefore, membrane M-6 was selected for further

analysis in permeation experiments because of its relatively stable and promising pervaporation performance.

A series of experiments with kerosene (1650 ppmw S) were carried out based on the statistical experiment design. The experimental results can be presented here as the following graphic plots which are accomplished with the software STAVEX 5.1 from company AICOS (Figure 3).

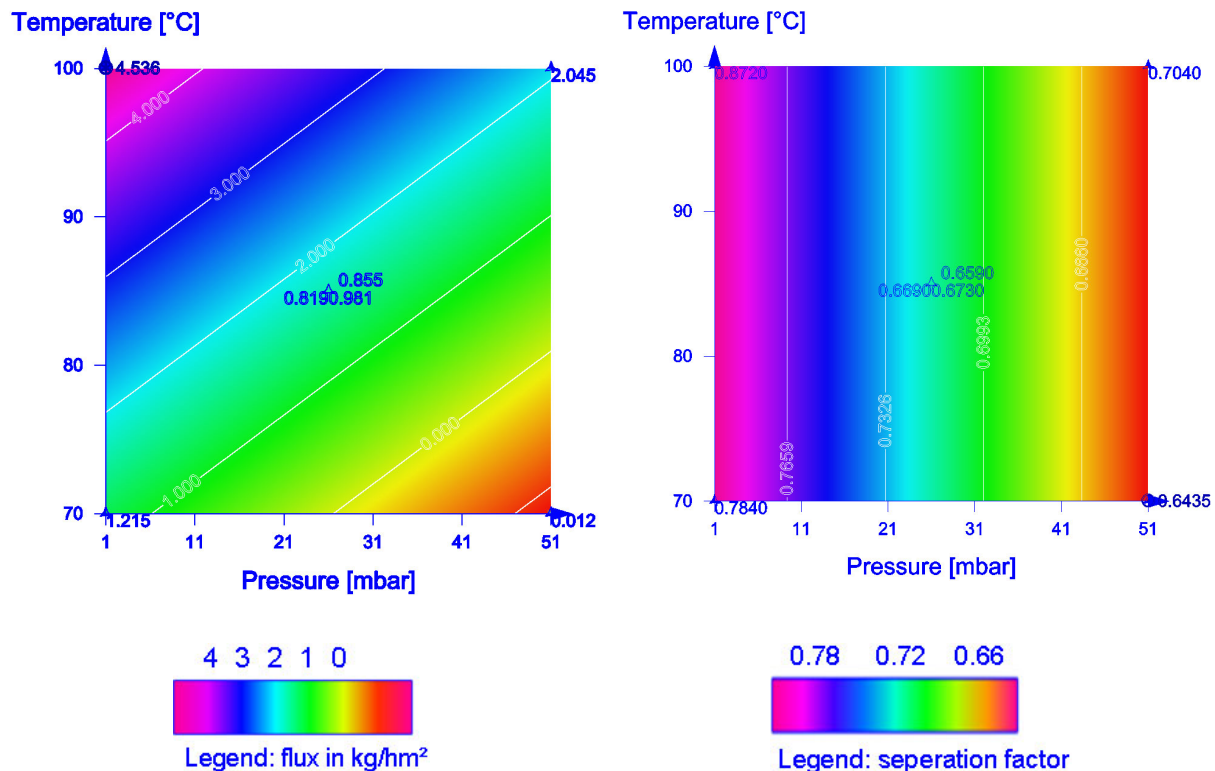


Figure 3: Results of statistical analysis in regard to the permeate flux J_p and the separation factor β in the ranges studied $70\text{ }^\circ\text{C} < T_{\text{feed}} < 100\text{ }^\circ\text{C}$ and $1\text{ mbar} < p_{\text{per}} < 51\text{ mbar}$; membrane M-6 with kerosene 1650 ppmw S; permeate temperature $T_{\text{per}}: -11\text{ }^\circ\text{C}$.

In the ranges studied for membrane M-6, i.e. $70\text{ }^\circ\text{C} < T_{\text{feed}} < 100\text{ }^\circ\text{C}$ and $1\text{ mbar} < p_{\text{per}} < 51\text{ mbar}$, the feed temperature (T_{feed}) and the permeate pressure (p_{per}) have a significant influence on the permeate flux and the separation factor. It can be seen that large separation factors and high permeate fluxes using membrane M-6 were obtained at low permeate pressures and high feed temperatures. Therefore, it is not possible to determine optimal operating conditions which lead to a low separation factor and a high permeate flux coincidentally. Considering the energy demand in an industrial application the economical operating conditions are determined here as a feed temperature of $90\text{ }^\circ\text{C}$ and a permeate pressure of 25 mbar . Under these conditions a separation factor of 0.71 and a corresponding permeate flux of $2.26\text{ kg h}^{-1}\text{ m}^{-2}$ were attained.

A different separation property was observed in the pervaporation of a light fraction of Jet A-1 with 290 ppmw S through the polyimide membrane M-5. At a permeate pressure of 4 mbar and a feed temperature of $134\text{ }^\circ\text{C}$ a separation factor of 3.08 was achieved through

membrane M-5 with 50% light cut of Jet A-1 provided by thermal distillation. The corresponding permeate flux was $0.38 \text{ kg h}^{-1} \text{ m}^{-2}$. This permeation potential provides another possibility for removing sulfur components by producing a retentate that has a lower sulfur content. Furthermore, in an industrial application a multi-stage membrane separation process is very attractive. The first step can be achieved by a polyurethane membrane with a sulfur reduction on the permeate side. Then the low sulfur fraction is fed to the subsequent step, in which a polyimide membrane with the opposite pervaporation behavior is employed to enrich the sulfur content on the permeate side. Future efforts on the second pervaporation step will firstly aim at screening more polyimide membranes and optimizing their pervaporation performance.

4 Adsorption Experiments

The low sulfur permeate fraction obtained with pervaporation experiments was supposed to be desulfurized subsequently by adsorption. However, since only a limited amount of permeate was collected from the permeation test rig, diverse light fractions of Jet A-1 produced by distillation were employed as analog permeate fractions. Analyses revealed that the substantial composition of both fractions is comparable.

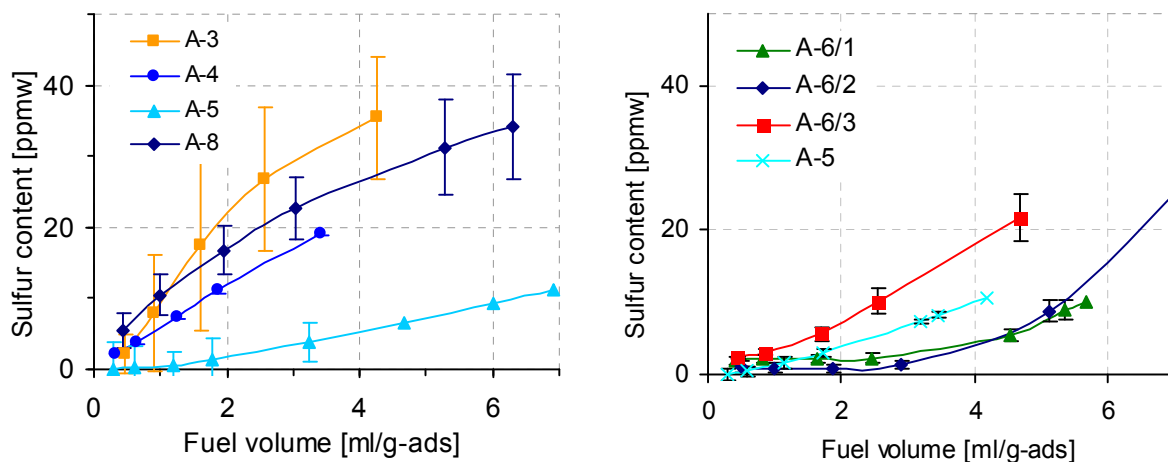


Figure 4: Adsorbent screening with 50% (vol.) light fractions of Jet A-1 (left: 290 ppmw S; right: 440 ppmw S); adsorption temperature T_{ads} : 20 – 140 °C; LHSV*: 1 h^{-1} ; regeneration temperature T_{reg} : 500 °C; heating time t : 3 h and GHSV*: 655 h^{-1} ; cumulative breakthrough curves obtained with consecutive desulfurization cycles (results with 95% confidence intervals).

A regeneration process with subsequent adsorption is denoted as an adsorptive desulfurization cycle. Multiple cycles were carried out consecutively to prove the reproducibility of the experiments. Figure 4 demonstrates the adsorption behavior of the eight most effective adsorbents from our laboratory experiments in operation with two kinds of 50% (vol.) light fraction of Jet A-1 having 290 ppmw and 440 ppmw S, respectively. Corresponding to the cumulative sulfur content of 10 ppmw 1 gram of adsorbent A-3, A-4, A-5, or A-8 is capable of treating 1.05, 1.65, 6.3, or 0.95 ml of 50% (vol.) Jet A-1 with 290

ppmw S, respectively, while 1 gram of adsorbent A-5, A-6/1, A-6/2, or A-6/3 is capable of treating 4.03, 5.68, 5.35, or 2.55 ml of 50% Jet A-1 with 440 ppmw S.

The best breakthrough adsorption capacity W_s of 1.93 mg S/g of adsorbent is obtained with adsorbent A-6/1, while A-3, A-4, A-5, A-6/3, and A-8 offer capacities of 0.23, 0.37, 1.52, 0.89, and 0.21 mg S/g of adsorbent, respectively. The consecutive desulfurization cycles with adsorbent A-6/1 did not exhibit any observable loss in sorbent breakthrough capacity, which is remarkable and is ideal for cyclic processes. Additionally, adsorbent A-6/2 is also considered to be a promising adsorbent with a sulfur capacity of 1.89 mg S/g of adsorbent. Therefore, in designing the adsorption process adsorbent A-6/1 was employed to optimize the operating conditions.

To optimize the adsorption and regeneration behavior, a series of experiments were performed with adsorbent A-6/1 and a 50% (vol.) light fraction of Jet A-1 containing 440 ppmw S on the basis of the statistical experiment design. According to the experimental results the sulfur adsorption capacity W_s and the percentage of sulfur removal in the regeneration process can be expressed as the following graphic plots in the ranges studied (Figure 5):

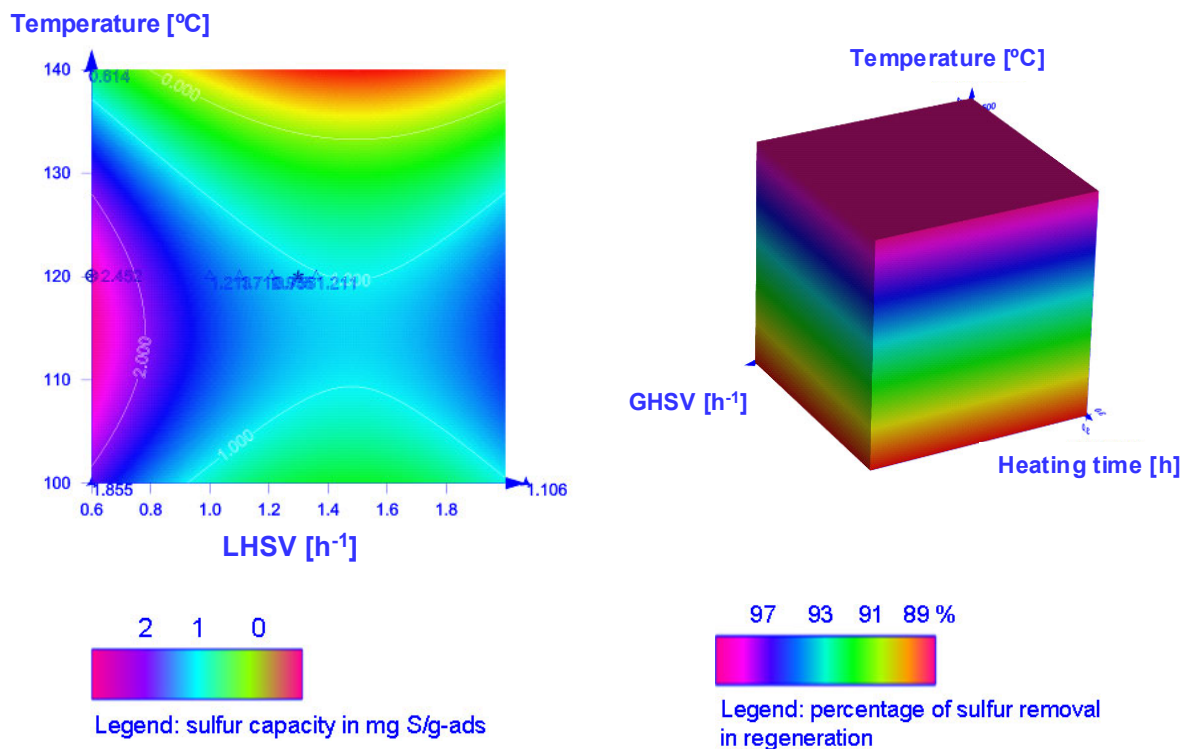


Figure 5: Results of statistical analysis for adsorbent A-6/1 with 50% light fraction of Jet A-1 having 440 ppmw S; left: influence of adsorption temperature T_{ads} and LHSV on the adsorption capacity W_s , $100\text{ }^\circ\text{C} < T_{ads} < 140\text{ }^\circ\text{C}$, $0.6\text{ h}^{-1} < \text{LHSV} < 1.8\text{ h}^{-1}$, $T_{reg} = 500\text{ }^\circ\text{C}$, $t = 3\text{ h}$, $\text{GHSV} = 655\text{ h}^{-1}$; right: influence of regeneration temperature T_{reg} , heating time t and GHSV on the sulfur removal in regeneration process, $400\text{ }^\circ\text{C} < T_{reg} < 500\text{ }^\circ\text{C}$, $1\text{ h} < t < 3\text{ h}$; $100\text{ h}^{-1} < \text{GHSV} < 655\text{ h}^{-1}$, $T_{ads} = 120\text{ }^\circ\text{C}$, $\text{LHSV} = 1\text{ h}^{-1}$.

Both of the adsorption temperature and LHSV influence the adsorption capacity in the range studied, as illustrated in the left graphic in Figure 5. The highest sulfur adsorption capacity of 2.45 mg S/g of adsorbent was obtained with an adsorption temperature of 120 °C and an LHSV of 0.6 h⁻¹. Considering the operating conditions in industrial applications, the optimal adsorption temperature and LHSV are determined as 120 °C and 1 h⁻¹, respectively.

The graphic cube in Figure 5 demonstrates that the percentage of sulfur removal in the regeneration process ranges from 97% to 100%. The improved sulfur adsorption performance can be achieved by an increase in the regeneration temperature T_{reg} , the heating time t and the GHSV of the treatment air. The consecutive desulfurization cycles indicate that the adsorption capacity can be fully recovered by regeneration at 500 °C for 3 hours with GHSV of 655 h⁻¹, which is regarded as the optimum regeneration condition.

As an economical alternative, the regeneration process may be accomplished at 450 °C for 2 h with a GHSV of 200 h⁻¹ resulting in a 10-20% reduction in the breakthrough adsorption capacity. Since under these conditions, less energy and a smaller amount of regeneration gas are required, this alternative will be chosen for operating conditions in a pilot plant.

5 Conclusions

In this study, liquid phase desulfurization of jet fuel by a combined pervaporation and adsorption process was examined. Seven different membrane materials and ten sorbent materials were screened to choose the most suitable candidates. Laboratory experiments were conducted to optimize the operating conditions and to collect data for a pilot plant design. As a result, Kerosene containing 564-1650 ppmw S can be desulfurized by membrane separation with a reduction of up to 50%. Subsequently, the fixed-bed adsorption process with integrated sorbent regeneration is able to reduce the sulfur content in the pre-treated fraction to less than 10 ppmw.

More experiments in regard to multi-membrane separation and multi-bed adsorption will be carried out in the laboratory at IEF-3. As the next step a combined process of pervaporation and adsorption for kerosene desulfurization will be installed as a pilot plant in the 5 kW class.

References

- [1] D. Dagget, J. Freeh, C. Balan, D. Birmingham. Fuel Cell APU for Commercial Aircraft, Proceedings Fuel Cell Seminar, Miami Beach, U.S.A., 2003.
- [2] T. Grube, R. Menzer, R.C. Samsun, J. Pasel, R. Peters. Optionen und Herausforderungen des Einsatzes von Auxiliary Power Units in mobilen Anwendungen, VDI-Berichte No. 1975, 2006.
- [3] S. Specchia, A. Cutillo, G. Saracco, V. Specchia, Concept study on ATR and SR fuel processors for liquid hydrocarbons, Ind. Eng. Chem. Res. 45 (2006) 5298–5307.
- [4] J. Pasel, J. Meißner, Z. Porš, R.C. Samsun, A. Tschauder, R. Peters. Autothermal reforming of commercial Jet A-1 on a 5 kW_e scale, International Journal of Hydrogen Energy, Vol. 32, 2007.
- [5] J. Hagen. Technische Katalyse – Eine Einführung, Weinheim, 1996.

- [6] W. Benz. Einfluss von Schwefelverbindungen in flüssigen Kohlenwasserstoffen auf ein Brennstoffzellen-Gesamtsystem am Beispiel eines katalytischen Crackers mit nachgeschalteter PEMFC, PhD thesis, University of Duisburg, 2005.
- [7] Zehnte Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes (10. BImSchV) vom 24.6.2004, BGBl. I No. 30 2004, pp. 1342 – 1347.
- [8] Ministry of Defence: Defence Standard 91-91; Turbine Fuel, Aviation Kerosine Type, Jet A-1, Nato Code: F-35, Joint Service Designation: AVTUR, Issue 5, United Kingdom of Great Britain and Northern Ireland, 2005.
- [9] C. Song. An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel, *Catalysis Today*, Vol. 86, 2003.
- [10] I.V. Babich, J.A. Moulijn. Science and technology of novel processes for deep desulfurization of oil refinery streams: a review, *Fuel*, Vol. 82, 2003.
- [11] R. Peters, J. Latz, J. Pasel, D. Stolten, Desulfurization of Jet A-1 and heating oil: general aspects and experimental results, *ECS Transact.* 12 (1) (2008) 543–554.
- [12] J. Balko, G. Bourdillon, N. Wynn, Membrane separation for producing ULS gasoline, *PTQ Spring* (2003) 17–25.
- [13] L.S. White, R.F. Wormsbecher, M. Lesemann, Membrane separation for sulfur reduction, Patent: US 2004/0211706 A1 (2004).