HYDROGEN PRODUCTION FROM SELECTED KEROSINE COMPONENTS BY PARTIAL CATALYTIC DEHYDROGENATION

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Abstract

The providing and storage of hydrogen for efficient fuel cell systems is an on-going challenge. The partial catalytic dehydrogenation (PCD) of liquid fuels can provide stationary or mobile fuel cell systems with hydrogen. Through PCD, liquid fuels can be treated as hydrogen storage as well as an energy provider for combustion processes. It is also an alternative to the common reforming processes where the fuel is converted with steam into a hydrogen rich product gas with co- products like carbon monoxide and carbon dioxide that requires CO clean-up before feeding into a proton exchange membrane fuel cell. The direct dehydrogenation on a catalyst can provide a hydrogen product gas of high purity (95 vol-%) without carbon monoxide or carbon dioxide.

The hydrogen is partly removed and the fuel is not completely transformed into a gaseous product. Therefore the partial dehydrogenated fuel can be used for further processes.

At the Institute of Technical Thermodynamics of the German Aerospace Centre, a test rig was built for the PCD of kerosene, to investigate the product gas quality, the by-products, and hydrogen yield.

A big challenge for PCD catalyst is the sulphur content, on average 500 ppmw, of kerosene [1]. To remove sulphur components from kerosene, thermal fractionation by rectification is suitable based on the boiling range of kerosene.

The process concept for the PCD with fuel cell system includes the desulphurization of kerosene or the use of desulphurized kerosene (DK) (3ppmw sulphur).

Keywords: Hydrogen, Kerosene, Dehydrogenation, Fractionation, Rectification

1. Introduction

The partial catalytic dehydrogenation of kerosene can be an alternative process for the hydrogen supply for fuel cell systems. Those systems could replace gas turbines as the auxiliary power unit (APU) on aircrafts. A fuel cell system has the potential of a high electrical efficiency, thereby reducing the fuel consumption and emissions of a conventional APU, which has an average electric efficiency of 15 % and causes 25 % of combustion emissions while on-land operations [2]. The first process concept being investigated consists of desulfurization of the kerosene by thermal fractionation, the dehydrogenation of the kerosene fraction, gas cleaning and a proton exchange membrane fuel cell (PEM) Fig.1.

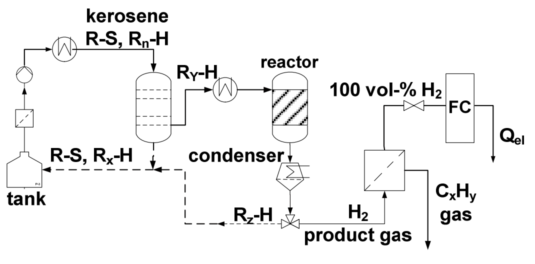

Figure 1 *process concept of PCD including fractionation, gas cleaning and fuel cell system*

The second concept utilizes desulfurized kerosene which allows direct dehydrogenation without fractionation as pre-treatment.

The experimental results of kerosene fractionation, the dehydrogenation of those fractions and desulfurized kerosene (DK) and single kerosene components are presented here.

2. Rectification of Kerosene

Kerosene is a very complex mixture of hydro carbons in the range of C7 up to C18. The chemical composition can also vary from batch to batch. For the investigation, the chemical structure of a batch of Jet A1 was analysed with GCMS (Agilent Thermo T230L Trace DSQ Turbo 250L sec 230) qualitatively and GCFID (Shimadzu GC2010) for quantitative definition. The kerosene contains more than 300 components of which 77.4 % of the detected area is identified. The average molecular formula of the analysed Jet A1 is $C_{10.7}H_{20.5}$ with an average molar weight of 148g/mol.

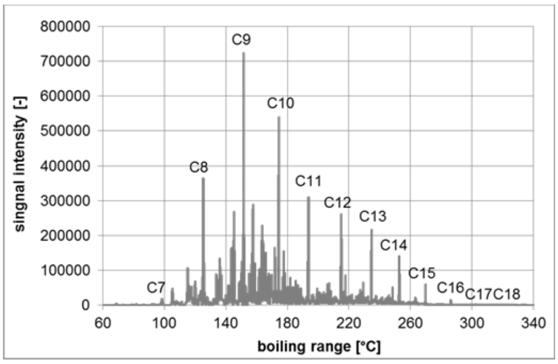

Figure 2 *GC-FID Chromatography of kerosene Jet A1*

The sulphur content was analysed with an elemental analyser (AnaltytikJena multi EA 5000) and measured to be 230 ppmw.

The fractionation is accomplished in a lab scale batch rectification with a Vigreux column. The kerosene Jet A1 is provided in a glass flask at the bottom of the rectification column. The heat is provided by 600 Watt electric heater. For the fractionation of 15 mass-% of the kerosene, the rectification runs at atmospheric pressure. For higher mass fractions the pressure is reduced by a vacuum pump in the rectification column.

The kerosene components of lower boiling range evaporate first. The Vireux column enforces a more defined separation of the components by the boiling temperature. With higher boiling temperature more kerosene mass is evaporated from the flask. After the column the evaporated kerosene compounds are condensed and collected. The fractions are defined by the mass evaporated from the kerosene flask.

Most sulphur in kerosene is bound to aromatic and polyaromatic hydro carbons which are benzothiophens and dibenzothiophens.[3].

These compounds appear in the higher boiling range of Jet A1, which allows a decreasing of the sulphur content by distillation.

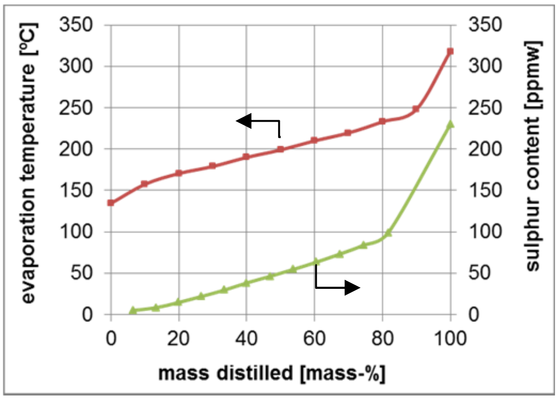

Figure 3 *boiling range and sulphur content in destillt mass of fuel of rectification*

Beside the sulphur content, the chemical composition of the fractions changes, depending on the mass fraction. The compounds are organized in hydrocarbon groups, n-alkanes, iso-alkanes, cylcloalkanes, dicycloalcanes, aromatic hydrocarbons and di aromatic hydrocarbons. Figure 3 shows the composition of the original Jet A1, the 15 mass-% Fraction, the desulfurized kerosene (DK), and the surrogates defined for the process simulation.

The compositions of the surrogates are designed to reproduce the chemical composition, the molecular weight, and the boiling range. However, the accessibility of defined components for experimental investigations limits the selection of components.

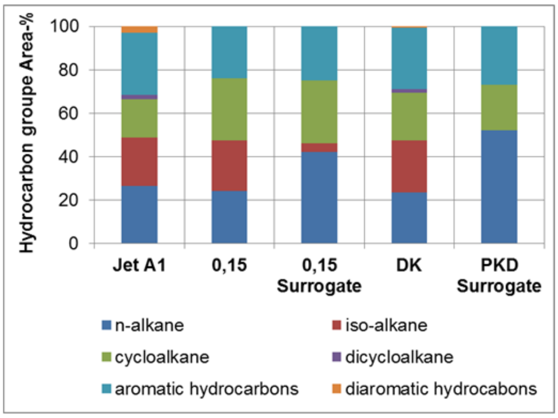

Figure 3 *compsition of hydrocarbon groups analyzed with GCFID and surrogates.*

3. Experimental methodology of PCD

The PCD (partial catalytic dehydrogenation) reaction was performed in a 15 mm ID stainless steel fixed bed tubular reactor. The reactor is electrically heated and operated between 350 °C and 500 °C. The catalytic bed material consists of 1.8 mm spherical γ-Al_2O_3 Pellets coated with Pt and Sn (Johnson Matthey).

The feed (20-30 g/hr) is evaporated and flows through the catalytic bed material. After passing through the reactor, the product stream is fed into a counter current heat exchanger, where ethanol at -10 °C condenses the condensable products which are the partly dehydrogenated kerosene components. The gaseous products are separated in the condenser from the fuel. The composition of the product gas is measured with a thermal conductivity detector (TCD) (ABB Caldos 27 AO2020) and with a GC-TCD (Varian GC4900) where the hydrogen and gaseous hydrocarbons (CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}) concentrations are measured. The condensate product is analysed with GC-FID.

Before applying the kerosene, the catalyst was reduced under hydrogen flow at 350°C for 2h.

The reaction conditions for desulfurized kerosene and kerosene fractions are investigated at a temperature of 450 °C [4] with various pressures and contact times (ct). The contact time is defined as the time on stream of the feed at reaction conditions though the porous catalyst bed (1). The porosity of the catalyst (ϕ) bed is 38%.

$$ct[s] = \frac{V_{catalyst\ bed} \cdot \Phi_{caltyst\ bed} \cdot R \cdot T}{\dot{m}_{Feed} \cdot p} \qquad (1)$$

The experiments were performed to define the reaction conditions for high hydrogen yield which is defined as the hydrogen produced per mass of feed ($nl_{H2}\ kg_{Feed}^{-1}$). Furthermore, the coke formation, and hydrogen purity were investigated. Before the experiment, the test rig was filled with nitrogen. The pressure of 1 and 5 bar, the contact time of 1.4 and 4 s and the influence of a hydrogen co-feed to the reaction was investigated.

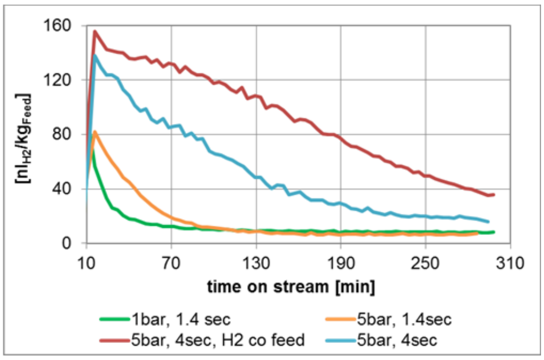

Figure 5 *hydrogen yield from PCD of DK at 450°C*

The hydrogen yield is increased by increase of pressure (up to 5 bar) and increase of contact time (up to 4 sec). However, the hydrogen yield is declining throughout the experiment time of 5 h, indicating a deactivation of the catalyst. This is caused by coke formation on the catalyst, (Table 1). This effect can be reduced by a 7 mol-% hydrogen co-feed.

	1 bar	5 bar	5 bar	5 bar
	1.4 sec	1.4 sec	4 sec	4 sec
	-	-	-	H_2 Co-Feed
gC/kgFeed	1.6	1.6	6.3	2.3

Table 1 *carbon distribution on catalyst from DK after 5h of PCD*

The hydrogen purity of the stream is stable in time between 85 vol-% and 90 vol-%. The PCD of the kerosene fractions was accomplished at the conditions of 450 °C, 5 bar, 4 sec contact time, and 7 mol-% H_2 co-feed. These conditions were defined to achieve highest hydrogen yield. Additionally to coke formation on the catalyst the gas composition shows cracking products of gaseous hydrocarbons.

The average Hydrogen purity of the product gas during 5 hrs is shown in Table 2.

Feed	H_2 purity [vol-%]
5 mass-%	88.2
15 mass-%	87.5
30 mass-%	87.4
DK	88.4

Table 2 *hydrogen purity from PCD of Jet A1 fractions and DK at 450°C*

Comparing the hydrogen yield results, the 5 mass-% fraction and the DK show the highest result. Both feeds have similar sulphur content. However the 5 mass-% fraction shows more cycloalkanes, which are much more likely to dehydrogenate than the other compound groups.

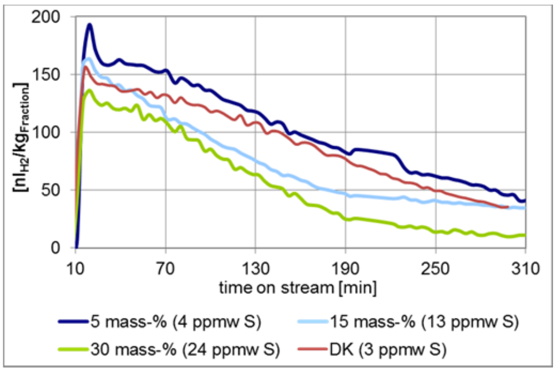

Figure 6 *hydrogen yield from PCD of Jet A1 fractions and DK at 450°C*

The liquid hydro carbon condensate of the 5 mass-% fraction was analysed with GC-FID. The comparison of the chromatography before and after PCD shows that cycloalkanes are reduced by 11 mass-% while aromatic hydrocarbons gain by the same amount, which would be dehydrogenation products. The n-alkanes and iso-alkanes show less than 3 % change. This can be caused by cracking into short chained alkanes.

To achieve higher H_2 purity and less coke formation on the catalyst, adaptations to the evaporation and the reactor were accomplished. Furthermore, the start-up strategy of the experiment was changed. The feed stream is slowly increased, instead of a hydrogen co- feed in a nitrogen atmosphere, the system is pressurised with hydrogen.

These changes decline the coke formation on the catalyst. The results with DK at 450 °C, 5 bar, and 4 sec of contact time show a significant difference in the gas composition. The coke formation from the DK was reduced by 40%, but it still leads to a strong deactivation of the catalyst bed.

Product gas composition	[vol-%]	adapted [vol-%]
H_2	88.4	97.4
CH_4	5.7	1.1
C_2H_6	0.0	0.8
C_2H_4	3.9	0.1
c_3H_8	2.0	0.6
C_3H_6	0.0	0.05

***Table 3** product gas composition of dehydrogenation of DK before and after adaptations of the experiment*

The influence of cracking and coke formation as side reactions to the dehydrogenation are important for the stability of the process and product gas quality.

The compound groups show very different behaviour in dehydrogenation. While n-alkanes and iso-alkanes tend to crack and probably cause the coke formation, aromatic hydrocarbons are practically inactive. Cycloalkanes are responsible for most of the hydrogen yield.

To investigate this hypothesis, tests with single components from a 15 mass-% fraction and DK surrogate are carried out. The aim is to understand the influence of the reaction conditions on the coke formation and the hydrogen yield of the component groups.

At first, decane is examined as representative of the n-alkane compound group. The reaction conditions are chosen at 1 bar and 2 sec contact time, while the temperature is varied from 350 °C to 500 °C.

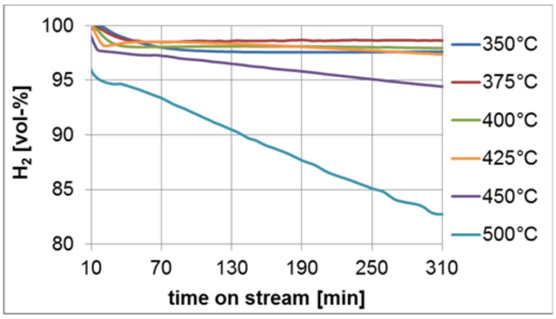

***Figure 7** hydrogen purity at temperature sensitvity test of decane*

In the temperature range from 350 °C to 425 °C, the hydrogen purity remains above 95 vol-% throughout the experimental time of 5 hrs, see Fig. 7. Above a temperature of 450 °C, the gaseous side products increase rapidly with time. This is caused by the coke coating the catalyst, which prevents dehydrogenation reactions. However, the thermal cracking of the decane is enhanced at higher temperatures, Table 4.

Temperature [°C]	Coke formation [gC/kgDecane]	Conversion [%]
350	0.4	3.0
375	0.7	5.8
400	1.0	6.9
425	0.8	9.4
450	1.7	13.7
500	4.2	25.3

***Table 4** temperature sensitivty tests of decaneshowing Coke formation on thecatalyst and decane conversion rate*

With increasing temperature the coke formation and the decane conversion show the same tendency. With higher temperature more cracking appears.

4. Conclusion

The PCD of kerosene can supply product gas of high hydrogen purity. The reactions are highly dependent on the hydrocarbon groups contained in the kerosene. The formation of coke is causing a strong deactivation on the catalyst which has to be reduced or removed to enable a stationary process.

5. Further work

The investigation of the dehydrogenation reactions of component groups is the central task to define conversion rates and reaction products to under the mechanisms of PCD of a complex mixture like kerosene. Furthermore, reduction of coke formation by adjusting the operating conditions is a central issue.

6. References

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