Comprehensive analysis of FT product with GCxGC

Matthys Janse van Vuuren*, Riaan Bekker, Thelma Grobler Sasol Technology R&D (Pty) Ltd., P. O. Box 1, Sasolburg, 1947, South Africa *Matthys.jansevanyuuren@sasol.com

Introduction

The analysis of FT product is well reported in literature. Unfortunately the focus is almost always on the paraffins and olefins and do not include the oxygenates. The first proper oxygenate distribution is reported by Teng et alⁱ and kinetics for the formation of oxygenates was discussed. It is clear from the reported data that the reported acids and the models do not correlate due to deviations in the analysis of higher acids. Furthermore there are oxygenates other than alcohols and acids in the FT product.

The mechanism of oxygenate formation in FT is a subject of various discussionsⁱⁱ. Co-feeding of oxygenates to determine re-adsorption / mechanism of secondary reactions is also a contentious subjectⁱⁱⁱ. (Unfortunately the comprehensive analysis of oxygenates are elusive due to analytical constrains and only partial analysis was possible.) The development of GCxGC technique has opened the door for better analysis of very complex feed streams^{iv}. This work reports on the development of a GCxGC technique for the comprehensive analysis of a very complex FT product. Due to the complexity of the product spectrum, numerous analyses were done to obtain the final product distribution.

Various oxygenates previously unknown in Fe-LTFT as well as the chain length distribution were determined and is reported here. Results indicate that the same mechanism is at play for the formation of the various classes.

Experimental:

The experimental procedure for catalyst preparation has been described previously^v. For this study, a catalyst with K₂O loading of 4.8/100Fe was used. The Reactor setup was also previously disclosed^{vi}. Briefly, Synthesis gas (H₂+CO, H₂/CO = 1.5) with 10% argon as internal standard, was continuously fed to a Continues Stirred Tank Reactor (CTSR), (600ml internal volume), filled with a suspension of catalyst (10g) and Fischer Tropsch wax (350g). The product from the CSTR went through two knock-out vessels 200°C and 25°C respectively before the gas was depressurised over a back pressure regulator to atmospheric pressure. The reactor was operated at 245°C and 26.5 bar absolute pressure. Before FT synthesis, the catalyst was activated with synthesis gas. The product analysis was done as disclosed earlier. FT product before the hot knock-out vessel was analysed with a GCxGC (Agilent 6890) from Zoex Corporation.

Results and discussion

Figure 1 shows the Anderson-Shultz-Flory (ASF) plot for the linear acids, nalcohols and total product as analysed with the multi dimensional GC. It is clear that the total product shows a two alpha distribution with a break between C_8 and C_{10} . Furthermore, the alpha 1 is similar for the total product, n-alcohols and acids.

Table 1. Alpha val	lues for compound classes.
--------------------	----------------------------

	Alpha 1	Alpha 2
total product	0.59	0.93
n-alcohols	0.60	0.82
linear acids	0.58	-

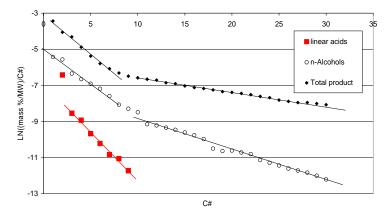


Figure 1. Anderson – Shultz – Flory plot for hydrocarbon classes as determined by full analysis of the FT product

Significance

The development of a comprehensive analysis of FT product highlights the possibility to verify the mechanistic aspects of Fischer-Tropsch. This knowledge will help in the design of more selective catalysts.

References

ⁱ B. Teng, C. Zhang, J. Yang, D. Cao, J. Chang, H. Xiang, Y. Li, *Fuel*, 84, 791-800, (2005) ⁱⁱ M. E. Dry, The Fischer-Tropsch Synthesis, Catalysis-Science and Technology, (J.R. Anderson, M. Boudard Eds.), Vol. 1, p.160. Springer Verslag, New York, 1981

ⁱⁱⁱ M. J Janse van Vuuren, South African patent application 2006/08515

^{iv} J. Dallüge, J. Beens and U.A.Th. Brinkman, J. Chromatogr. A, 1000, 69-108, (2003)

^v M J. Janse van Vuuren, G. N. S. Govender, R. Kotze, G. J. Masters and T. P. Pete; "The correlation between double bond isomerization, water gas shift and acid production during Fischer-Tropsch synthesis; ACS Div. Petroleum Chem. Preprints, 50(2), 200-2002 (2005) vi, N.S. Govender, M. Janse van Vuuren, M. Claeys, E. van Steen, http://dx.doi.org/10.1021/ie060415e