

# NMR Studies of the Phase Behaviour of Fischer-Tropsch Reaction Product Mixtures Confined in Mesoporous Media

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## Highlights

- Hydrocarbon-in-water emulsion confined in mesopores of diameter 14, 20, 25 and 39 nm.
- Droplet sizes are much larger than pores, and coalesce significantly in 14 nm pore diameter.
- Water is surface wetting phase when only saturated alkane present in hydrocarbon phase.
- In presence of stearic acid, wetting phase is water in pores  $\leq 20$  nm, hydrocarbon in pores  $\geq 25$  nm.

## 1. Introduction

Fischer-Tropsch (FT) synthesis produces saturated linear hydrocarbons as the main desired product. Water is the major reaction by-product. In industrial fixed bed reactors, both products form together *in situ* inside the pores of catalysts. FT catalysts are typically mesoporous, meaning the average pore diameter lies in the range of 2 - 50 nm. Oxygenated products such as *n*-alkanoic acids are minor products of FT, however they can have a significant effect on reaction conversion and selectivity. Specifically, alkanolic acids have been shown to form a hydrophobic layer near the catalyst pore surface, which hinders access of water to the active site, potentially leading to decreased catalyst deactivation. The presence of both saturated hydrocarbons and water products in the pores may lead to the formation of hydrocarbon-in-water emulsions under certain reaction conditions [1]. However, whilst previous experimental studies of mesoscopically-confined immiscible liquid mixtures have focused on the separation of two continuous liquid phases [2], none have addressed the presence of emulsions. In the present work, Pulsed-Field Gradient (PFG) NMR and NMR relaxometry are employed to investigate an *n*-octacosane-in-water emulsion confined in the mesopores of silica spherules of average pore diameter 14, 20, 25 and 39 nm. The variation in droplet size and the surface wetting species with pore diameter is studied. *n*-Octacosane is chosen as it represents the typical average chain length of FT products [3]. The inclusion of stearic acid in the emulsion mixture in all pore diameters is also investigated to understand the effect of a hydrophobic surface layer forming in the pores.

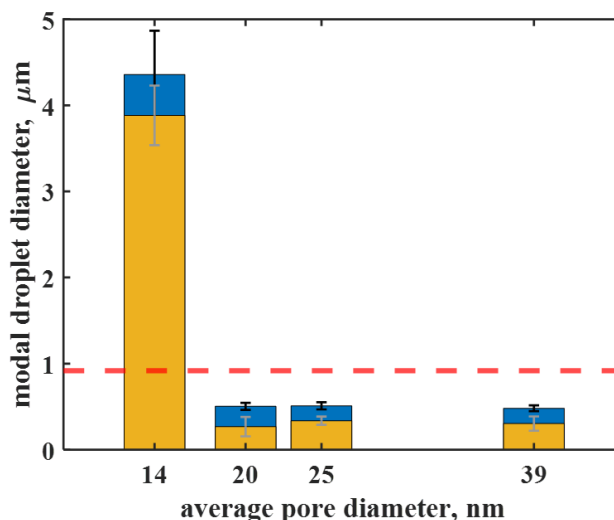
## 2. Methods

Bulk emulsions were prepared by ultrasonication of a 42 vol% *n*-octacosane and 58 vol% deionised water mixture for 1 h in a heated water bath at 80 °C. Silica spherules were then inserted into the emulsion for 1 h during which imbibition of the emulsion into the pore space occurred. For studies including stearic acid, the silica spherules were immersed in the acid for 30 min before being inserted into the emulsion. All NMR experiments were conducted on a Bruker spectrometer with a magnetic field strength of 7.1 T, at a temperature of 80 °C. The NMR signal derived from the hydrocarbon was spectroscopically isolated from water, enabling differentiation of the continuous water and discrete hydrocarbon phases in the emulsion. PFG NMR measurements were used to extract the droplet sizes using a well-established data processing methodology [4]. Inversion recovery spin-lattice relaxation time measurement experiments were used to probe the surface wetting phase. If the extracted spin-lattice relaxation time for a component in the confined mixture was smaller than its value when pure, the phase

formed by the component is surface wetting. If the spin-lattice relaxation time is larger than when the component was pure, the phase formed by that component is non-wetting, located away from the surface [5].

### 3. Results and discussion

**Figure 1.** The modal emulsion droplet diameter vs the average pore diameter of silica pores in which the emulsion is confined. The blue bar (and black error bars) represents data for when only *n*-octacosane and water are present, whilst the yellow bar (and grey error bars) represents data for when *n*-octacosane, water and stearic acid are present. Error bars represent the standard error computed from repeat experiments on the same sample. The dashed red line represents the modal droplet diameter of the bulk, unconfined emulsion.



Emulsion droplet sizes extracted by PFG NMR are given in Figure 1. Droplet diameters are at least 6 time larger, and up to 2 orders of magnitude larger, than the pore diameters, meaning the droplets are present as ganglia which penetrate multiple pores. The diameter of confined droplets in systems with and without stearic acid increases substantially as the average pore diameter decreases from 20 nm to 14 nm, consistent with a threshold diameter for droplet coalescence existing within this range of pore sizes. NMR relaxometry data are consistent with the continuous water phase being wetting for all pore diameters in systems with no stearic acid. When stearic acid is included in the emulsion, the data are consistent with the hydrocarbon droplets being the wetting phase for pore diameters of 25 and 39 nm, but water being the wetting phase for pore diameters of 14 and 20 nm. Therefore decreasing the pore diameter from 25 to 20 nm has induced wetting reversal.

### 4. Conclusions

The phase behavior of an emulsion mixture representative of FT reaction products that form *in situ* inside catalyst pores has been investigated using NMR when confined in silica mesopores. This work has revealed that the catalyst pore diameter can significantly influence the phase behaviour of the reaction mixture inside the catalyst pores. Such changes in phase behaviour would, in turn, be expected to influence catalyst conversion and mass transfer of FT reactants and products into and out of the catalyst pores. The magnetic resonance methods reported here provide an additional analytical tool to help optimize the design of FT catalysts for optimal conversion characteristics.

### References

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### Keywords

Emulsion; Fischer-Tropsch catalysis; Pulsed-Field Gradient NMR; NMR relaxometry