

## Supporting Information:

### Hydrogenation of oxidised wax and a process to produce olefins from paraffins by autoxidation, selective hydrogenation and dehydration

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#### Autoxidation of Fischer-Tropsch waxes

**Background.** Autoxidation of wax introduces oxygenate functionality into the hydrocarbons and allow the waxes to be emulsified for applications such as coatings, polishes and water-based inks.<sup>(1)</sup> Depending on the application, the autoxidation conditions are changed to target a specific set of properties in terms of alcohol, carbonyl, acid and ester content of the oxidised wax. For more background on this subject, the reader is referred to the excellent text by Asinger.<sup>(2)</sup>

**Laboratory batch autoxidation.** On laboratory scale the autoxidation of waxes are typically studied in batch-mode, although studies on continuous mode oxidation have been reported.<sup>(3)</sup> During batch-mode oxidation the operating conditions are typically kept constant. Air is continuously introduced through a sparger and bubble through the molten wax that is kept at a constant temperature in a glass batch reactor.

The preparation of the Ox-C105-type oxidised waxes used in the present study were typically performed at an air flow rate of  $2.3 \text{ L}\cdot\text{kg}^{-1}\cdot\text{min}^{-1}$  at around  $160 \text{ }^\circ\text{C}$ ,  $0.3 \text{ MPa}$  and for a duration of  $5\frac{1}{2}$  hours. Despite care being taken to ensure good repeatability of experimental conditions, there is generally some variation in the properties of the oxidised wax. The different batches of Ox-C105 prepared on laboratory scale were therefore characterised before use and the batch-to-batch variation will be apparent from the data in the manuscript.

**Commercial batch autoxidation.** Commercial batch-mode autoxidation differs from the laboratory autoxidation not only in scale, but also operating procedure. Since the first step in autoxidation (initiation) is slow, the autoxidation is generally performed in two steps, with the first phase being conducted at a higher temperature (Figure S1). Batch times may be pre-set, or controlled by analysis of the product. The duration of the second phase of the autoxidation is typically set to achieve a specific level of conversion as determined by the acid number<sup>(4)</sup> of the oxidised wax. Some wax grades are saponified to convert some of the acids to soaps at the end of the second phase of autoxidation (not shown in Figure S1).

The properties of the oxidised wax are mainly determined by the temperature programme, operating conditions and wax feed. Some variation is introduced by residual oxidised wax from the previous batch (affects initiation time), corrosion products (can catalyse autoxidation) and handling conditions on unloading and storage of the oxidised wax (further autoxidation). The production procedure and properties of some of the commercial grades of oxidised wax produced by Sasol are given in Tables S1 and S2.<sup>(1)(5)</sup>

In general the nature of batch-mode autoxidation is such that oxygen availability is not controlled and during the second phase carboxylic acids are produced (Table S2). Apart from the carboxylic acid functionality in the oxidised wax, oxidation also results in the formation of short chain carboxylic acids and other oxygenates. The short chain oxygenates are stripped from the oxidised wax by the air bubbling through the reactor and the off-gas is rich in oxygenates. These oxygenates and paraffins resulting from oxidative cleavage of the wax must be knock-out before the N<sub>2</sub>-rich air can be vented. The composition of the off-gas (Table S3) depends on the autoxidation severity. This stream is corrosive on account of the short chain carboxylic acids. In a Fischer-Tropsch refinery the condensed material can in principle be co-processed with the Fischer-Tropsch aqueous effluent, although it is not presently being done at the Sasol 1 site.

## **Acknowledgement**

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## **Literature cited**

(1) Le Roux, J. H.; Oranje, S. Eds. *Fischer-Tropsch waxes*; Sasol: Sasolburg, 1984.

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- (3) De Klerk, A. Continuous-mode thermal oxidation of Fischer-Tropsch waxes. *Ind. Eng. Chem. Res.* **2003**, *42*, 6545.
- (4) ASTM D 1386. *Standard test method for acid number (empirical) of synthetic and natural waxes*; ASTM: West Conshohocken, PA, 1998.
- (5) Indyka, I.; Dawes, L. Process proposal for the wax oxidation/saponification reactors for phase 1 of the expansion project; Sasol Technology Process Development report 94/NV/02, 1994.

**Table S1.** Production procedure for different commercial oxidised waxes according to the workflow shown in Figure S1.

Work- flow	Description	Oxidised wax grades			Saponified oxidised wax grades			
		A1	A6 <sup>(*)</sup>	A28.1	A2	A3	A14	A28.2
	Fe-LTFT wax feed	H2-wax	H2-wax	C105-wax	H2-wax	H2-wax	H2-wax	C105-wax
	Saponification chemical	none	none	none	LiOH	LiOH	Ca(OH) <sub>2</sub>	LiOH
(1)	Wax pre-heating time (min)	10-15	10-15	10-15	10-15	10-15	10-15	10-15
(2)	Autoxidation, phase 1 time (min)	80	80	80	80	80	80	80
	Autoxidation temperature (°C)	175	180	175	175	175	175	175
(3)	Wax cooling time (min)	40	0	40	40	40	40	40
(4)	Autoxidation, phase 2 time (min)	>80	>80	>80	>80	>80	>80	>80
	Autoxidation temperature (°C)	140	180	140	140	140	140	140
	Acid number (mg KOH/g)	27-29	35-45	27-29	21-23	25-28	25-27	21-23
(5)	Unloading temperature (°C)	100-120	130	110-130	110-120	120-130	100-120	110-120
Σ	Average batch time (min)	400	-	450	380	470	-	390

<sup>(\*)</sup> Highly oxidised wax, no nitrogen used during its production.

**Table S2.** Typical properties of different commercial oxidised waxes produced from Sasol Fe-LTFT derived H2- and C105-waxes. In practice considerable variation may be found in properties that are a strong function of the autoxidation, such as the ester number.

Property	LTFT wax feed		Oxidised wax grades			Saponified oxidised wax grades			
	H2	C105	A1	A6	A28.1	A2	A3	A14	A28.2
Acid number (mg KOH/g)	<0.1	-	27	37	28	11	10	7	12
Ester number (mg KOH/g)	-	-	28	65	27	14	24	26	-
Penetration at 25°C, ASTM D1321 (mm)	<0.1	<0.1	0.6	2.5	-	<0.4	0.25	0.2	-
Congealing point, ASTM D 938 (°C)	98	104	87	79	94	89	91	86	97
Melting point, ASTM D 127 (°C)	-	-	96.5	-	-	101	103.5	-	-
Latent heat of fusion (kJ/kg)	217	245	192	126	174	182	185	179	175
Specific heat capacity (kJ/kg.K)									
at 25 °C	1.8	1.9	2.3	3.1	2.2	2.5	2.1	2.6	2.1
at 130 °C	2.3	2.7	3.0	2.6	2.6	3.8	2.8	-	3.0
at 170 °C	2.5	2.8	2.9	2.6	2.5	3.8	2.6	1.6	2.8
Average molecular mass (g/mol)	785	1100	700	720	890	750	780	750	1090
Density (kg/m <sup>3</sup> )									
at 25 °C	940	950	950	950	940	960	980	980	960
at 100 °C	-	-	825	842	-	814	829	846	-
at 110 °C	-	-	819	830	810	805	824	836	-
at 120 °C	-	-	813	820	-	797	821	832	800
Viscosity (cP)									
at 125 °C	-	-	12	25	19	20	32	44	36
at 135 °C	6-10	18	10	20	16	14	22	38	28
at 145 °C	-	-	8.5	17	14	11.5	15	32	21
Surface tension at 130 °C (N/m)	-	-	0.0284	0.0291	0.0222	0.0288	0.0336	0.0294	0.0281

**Table S3.** Typical composition of the off-gas from batch-mode autoxidation of waxes. Normal operation refers to the production of oxidised waxes such as A1 and severe operation refers to the production of oxidised waxes such as A6.

Description	Normal operation	Severe operation
<i>Flow rate (kg·h<sup>-1</sup> per ton wax)</i>		
organics	9	19
water	27	52
air	1124	1089
<i>Organics composition (mass %)</i>		
alcohols	4	5
carbonyls	5	5
carboxylic acids	74	72
paraffins	12	13
other organics	5	5

**Figure S1.** Workflow of commercial batch-mode oxidised wax production. (1) The loaded wax is preheated to the autoxidation temperature under nitrogen. (2) The first phase of autoxidation takes place, which is mainly initiation during which hydroperoxides are formed. (3) The temperature is adjusted to the temperature for the second phase of autoxidation. (4) The second phase of autoxidation takes place, which is the main production phase during which the wax is functionalised. (5) The oxidised wax is cooled down under nitrogen for unloading.

