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Separation of Primary Alcohols and Saturated Alkanes from Fisher–Tropsch Synthesis Products

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ABSTRACT

A method for separating primary alcohols and saturated alkanes from the products of Fisher–Tropsch synthesis is developed. The separation scheme consists of three steps: (1) the raw material is pre-separated by fractional distillation into four fractions according to normal boiling points; (2) appropriate extractants are selected to separate the primary alcohols from the saturated alkanes in each fraction; (3) the extractants are recovered by azeotropic distillation and the primary alcohols in the extract phase are purified. Based on the proposed method, the total recovery rates of the primary alcohols and the saturated alkanes are 86.23% and 84.62% respectively.

1. Introduction

Although natural gas is a limited resource, the associated gas in the offshore oilfield is usually vented or burned directly, wasting resources and contaminating the environment. Recently, the conversion of associated gas into linear chain primary alcohols and saturated alkanes via Fisher–Tropsch synthesis has been reported [1–6]. With a Co-based catalyst applied because of its high activity, high selectivity for long chain paraffins and a low water gas shift activity [7,8], the Fisher–Tropsch synthesis produces a product with primary alcohols: hydrocarbon weight ratio close to 1:1 and the content of waxy hydrocarbons less than 5%, demonstrating great industrial potential.

The hydrocarbons in the Fisher–Tropsch product can be used as various fuels according to the number of carbon atoms, such as, liquefied petroleum gas (C_3–C_4), gasoline (C_5–C_{12}), diesel fuel (C_{13}–C_{22}), and light waxes (C_{23}–C_{33}). The primary alcohols in the product also have many industrial applications. For instance, higher alcohols, which contain more than six carbon atoms [9], are the primary material in synthesizing surfactants, washing agents, plasticizers and many other fine chemicals. In addition, derivatives of these higher alcohols have been widely used in spinning, papermaking, foodstuffs, pharmaceuticals, leather, building, mining, metallurgy, machinery and agriculture [10].

Separation of alcohols and alkanes has been extensively studied. Bonthuys *et al.* [11,12] studied the separation of alkanes and alcohols with supercritical fluids. Krishna and Van Baten [13] developed a method to separate linear alkanes and alcohols by using cage-type zeolites according to different saturation capacities. Mathys *et al.* [14] used pervaporation to separate long-chain 1-alkanols from the corresponding *n*-alkanes. Although these novel methods possess many advantages, such as high recovery rate and high product purity, they are not mature

Table 1
Composition and normal boiling points of the components in the raw material

Pri-alcohol	Mass composition/%	BP/°C	Sat-alkane	Mass composition/%	BP/°C
C_1 – OH	3.32	64.05	C_5	8.14	36.30
C_2 – OH	1.14	76.98	C_6	6.07	68.86
C_3 – OH	1.78	96.23	C_7	6.56	98.42
C_4 – OH	4.10	116.85	C_8	8.56	125.91
C_5 – OH	5.85	136.46	C_{10}	6.86	173.87
C_6 – OH	5.21	157.23	C_{11}	3.34	194.18
C_7 – OH	3.96	176.26	C_{12}	2.85	214.91
C_8 – OH	5.00	195.25	C_{13}	2.43	234.65
C_{10} – OH	4.88	230.56	C_{14}	3.02	252.93
C_{12} – OH	3.61	263.8	C_{16}	2.72	285.86
C_{14} – OH	2.78	294.05	C_{17}	1.63	301.11
C_{16} – OH	1.79	321.60	C_{18}	1.40	314.62
C_{18}—OH	0.56	346.62	C_{19}	1.11	327.84
			C_{20}	0.89	340.63
			C_{21}	0.44	356.50
Total	43.98		Total	56.02	

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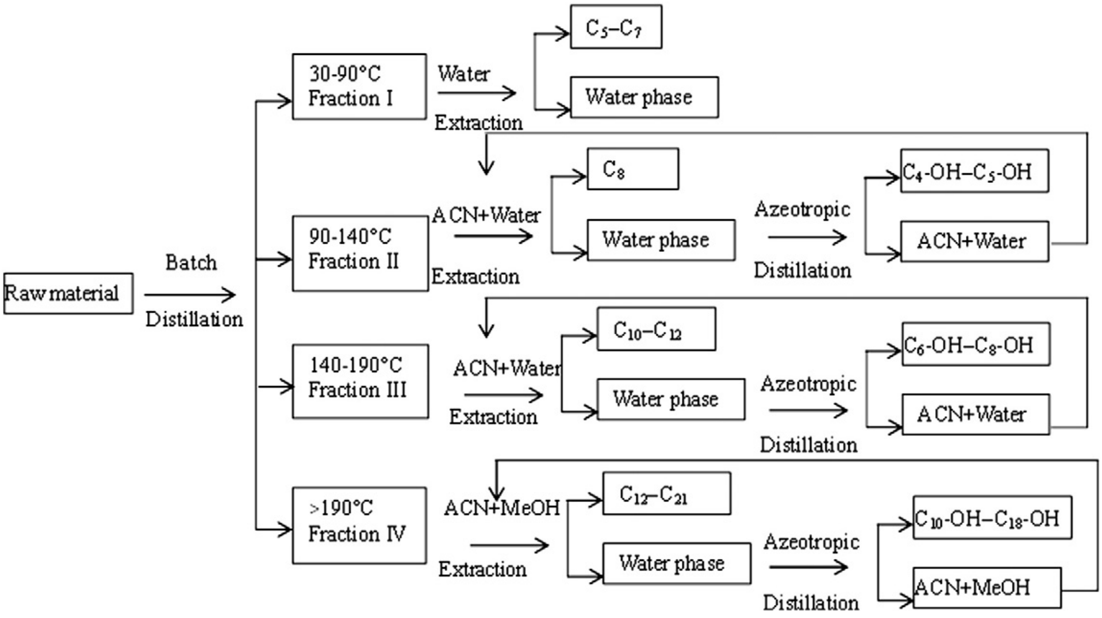

Fig. 1. Separation process of the experiment.

enough to be applied to industrial production. Therefore, a combined process of extraction and azeotropic distillation [15,16] for simultaneous recovery of primary alcohols and saturated alkanes from Fisher–Tropsch synthesis products is presented herein. This process can be readily converted to an industrial scale.

2. Raw Material and Separation Scheme

2.1. Raw material characteristics

The raw material was the mixture of products from a Fisher–Tropsch synthesis with a Co-based catalyst. The qualitative and quantitative analyses for the raw material were performed with the gas chromatographic method. The composition of the raw material and the normal boiling point [17] of each component are listed in Table 1. The primary alcohols account for a weight ratio of 43.98% and the saturated alkanes account for 56.02% of the raw material. The lowest normal boiling point (36.3 °C) is for *n*-pentane and the highest (356.5 °C) is for *n*-heneicosane, accounting for the wide boiling range of the raw material. The saturated alkanes are non-polar, whereas the primary alcohols are polar or weakly polar. Methanol has the strongest polarity and the polarity of alcohols decreases as the number of carbon atoms increase. The polarity of C_{18}-alkyl alcohols is so weak that it can form a stable and homogeneous solution with the non-polar saturated alkanes.

2.2. Separation scheme

Distillation is the most commonly used method to separate liquid mixtures, but it is not suitable for complete separation of mixed alcohols and mixed alkanes due to their similar volatilities. A hybrid separation scheme is proposed here to accomplish the separation. It includes three steps: (1) the raw material is pre-separated by fractional distillation into four fractions according to normal boiling points; (2) appropriate extractants and operating conditions are selected to separate the primary alcohols from the saturated alkanes and then extraction is performed on each fraction; and (3) the extractants are recovered by azeotropic distillation and the primary alcohols in the extract phase are purified. The separation process is given in Fig. 1.

2.3. Experimental equipment

A packed column with 3-mm-diameter Dixon packings was used in this separation process. The height and diameter of the column were 1200 mm and 25 mm, respectively. Liquid–liquid extraction was performed in a 500-ml separatory funnel. An Agilent Technologies 7890A GC System was employed to perform qualitative and quantitative analyses for each component in the distillation and extraction experiments. The gas chromatographic conditions are as follows: column of HP-5MS, 30 m × 0.25 mm, film 0.25 μm; flame ionization

Table 2
Compositions of the distillation fractions

Component	Mass composition/%			
	I (30–90 °C)	II (90–140 °C)	III (140–190 °C)	IV (>190 °C)
C_1-OH	11.35			
C_2-OH	4.34			
C_5	27.34	0.30		
C_3-OH	6.13	0.85		
C_6	21.68	0.44		
C_4-OH	3.20	16.06		
C_7	21.73	4.22		
C_5-OH		28.54	1.77	
C_8	4.22	39.76		
C_6-OH		4.45	15.02	
C_7-OH			17.24	
C_{10}		5.39	19.40	
C_8-OH			19.64	0.63
C_{11}			14.00	0.37
C_{12}			7.94	3.76
$C_{10}-OH$			3.55	13.96
C_{13}			1.44	7.88
C_{14}				11.30
$C_{12}-OH$				12.75
C_{16}				10.44
$C_{14}-OH$				9.88
C_{17}				6.04
C_{18}				5.16
$C_{16}-OH$				6.37
C_{19}				4.02
C_{20}				3.46
$C_{18}-OH$				2.05
C_{21}				1.92
Total	100.00	100.00	100.00	100.00