Thermal Cracking to Improve the Qualification of the Waxes

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Abstract: Thermal cracking of waxes at mild conditions (430-500\textdegree C) has been reconsidered as a possible refining technology for the production of fuels and chemicals. In this study, the more moderate thermal cracking was investigated to process Uinta Basin soft waxes to achieve the required pour point so that they can be pumped to the refineries. The best thermal cracking conditions were set 420 \textdegree C and 20 minutes. The viscosity and density of the final liquid product were respectively achieved as 2.63 mPa\textperiodcentered s and 0.784 g/cm\textsuperscript{3} at 40 \textdegree C. The result of FT-IR analysis of the liquid product indicated that the unsaturated hydrocarbons were produced after thermal cracking, which was corroborated by the \textsuperscript{13}C NMR spectrum. The GC analysis of the final gas product indicated that the hydrogen was produced; the dehydrogenation reaction was also proved by the elemental analysis and HHV results. The pour point of the final liquid product met the requirement.

1. Introduction
The decomposition of the waxes was normally accomplished by catalytic cracking with some cracking catalysts such as ZSM-5 at 500 \textdegree C or even higher temperature [1]-[5]. Calemma [6] processed the long chain n-alkanes with Pt/amorphous SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} catalyst and investigated the temperature range of 345-380 \textdegree C with the reaction time up to 32 h and the hydrogen pressure of 8.1 MPa when the catalyst concentration catalyst (g)/n-paraffin (mole) was 4.94. Not only high temperature but long reaction time was considered when Kyong-Hwan Lee [7] investigated the wax oil. The catalysts used for catalytic cracking are expensive and the catalysts should be separated from the products with some loss. The thermal cracking as a possible refining technology has many benefits, such as low gas production, without high-priced catalysts and hydrogen use, thus it is an effective and cheap way to deal with the waxes. Either to produce the fuels or chemicals, the waxes must be transported to the factories, but it’s inconvenient to accomplish for the soft waxes. Arno de Klerk [8] reported a method for thermal cracking of the hard waxes, and the operating temperature ranged from 420 to 500 \textdegree C with 0-6 MPa, and 0.1-1 h residence time, and the wax properties was found without significant change at temperatures below 400 \textdegree C after 1 h residence treatment. But as for the soft waxes, more moderate reaction conditions should be considered. In this study, thermal cracking was used to process the soft waxes to modify its fluidity qualification so that it could be much easier to transport from the field to refineries.

2. Experimental
2.1. Materials
The wax provided by Uinta Basin (UT, USA) is a kind of yellow soft paste without any fluidity at room temperature. It should be pumped to the refinery at the possible lowest temperature around 10℃ (the pour point should be lower than 10℃).

2.2. Equipment and procedure
A Parr 4848 high pressure reactor was used (Parr Instrument Company). In each experiment, wax (about 50g) was put into the reactor, then nitrogen was injected to flash the reactor; and the wax was heated up to the preset temperature and kept for various reaction times with stirring. The pressure variations with different reaction time at different preset temperatures were recorded. After the reaction, the reactor was cooled to room temperature and the residual pressures were recorded; meanwhile the final gas sample was also collected, and then the reactor was depressurized and opened to recover products for analysis.

2.3. Product analysis
Pour point was investigated by putting the cracked wax oil into a test tube (ISO 3016-1994) and cooled in ice bath until the temperature of the sample decreased to 2℃. The tube was inclined at an angle to check the liquid surface changed or not to judge if the sample passed the pour point test. The FT-IR spectrometer (Thermo Fisher Scientific Inc., Waltham, MA) was used to analyze the functional group changes before and after the cracking experiments, and a 300 MHz JEOL Carbon-13 Nuclear Magnetic Resonance (13C NMR) instrument (JEOL Ltd., Tokyo) was also used to identify the major functional groups present in the cracked oil. The viscosity and density were measured at 40℃ using SVM300 Stabinger Viscometer (Anton Paar Ltd.), and the API gravity of the liquid products were calculated from their specific gravities. Gas product was collected in Supel Inert gas sampling bags (Supelco), and analyzed by the SRI 8610C gas chromatograph (SRI Instruments, CA, USA). The carbon, hydrogen, nitrogen and sulfur contents of wax and final liquid product were determined by a FLASH 2000 Series CHNS/O analyzer (Thermo Fisher Scientific Inc., Waltham, MA), and oxygen was determined by difference. The higher heating values (HHV) of the liquid samples were detected by IKA 2000 basic bomb calorimeter (IKA Works, Inc., Wilmington, NC).

3. Results and discussion
3.1. The effect of the different temperature
According to the reference researches above, the waxes were processed at mild temperature 450℃ initially, and then the temperature was changed, basing on the product properties. The cracked oil from the reaction temperature at both 450℃ and 430℃ were complete liquid and passed the pour point without doubt, the reaction temperature could be reduced even further to 410℃, but the waxes paste was found in the reactor after the reaction, so the suitable temperature should be 420℃, the pour experiment also proved that. The results of the pour point tests of the products are shown in Table 1. It is obviously that pour point test is successful when temperature is over 420℃. Hence, the suitable reaction temperature is 420℃, which not only meet the requirement of the pour point test but also meet the energy conservation.

| Temperature,℃ | 450 | 430 | 420 | 410 |
|---------------|-----|-----|-----|-----|
| Passed the pour point or not (at 2℃) | Passed | Passed | Passed | Not passed |

The viscosity and density of the cracked oil were analyzed, and the results are shown in Figure 1. From 450℃ to 410℃, the viscosity of the product increase from 0.86mP·s to 3.67 mP·s. Especially when the temperature ranged from 420℃ to 410℃, the viscosity raise greatly from 1.85 mP·s to 3.67 mP·s, the latter is almost twice as much of the former. According to the viscosity variation, we find the right reaction temperature should be 420℃ too. The densities of the products from 450℃ to 410℃ vary from 0.761 to 0.790 g/cm³ which are all not very high.
Figure 1. The viscosity and density of the cracked oil at different reaction temperature (30 min). a: the effect of temperature to the viscosity of the product; b: the effect of temperature to the density of the product.

The pressures with the reaction time are described in Figure 2 and the residual pressures are recorded in Table 2. It shows that when the reaction temperature reach to the preset 450°C, 430°C, 420°C and 410°C, the corresponded pressures are 150psi, 110psi, 60psi and 50psi. All the pressures increase with longer reaction time at different preset temperatures, and the pressures after the reaction raise up to 250psi, 170psi, 140psi and 100psi which mean that there must be some thermal cracking reactions happened, and some more light compounds were produced, that’s why the pressures keep increasing with longer reaction time at the same reaction temperature. It also shows in Figure 2 that, the pressure 140psi after the reaction at 420°C is even lower than the pressure before the preset reaction time begins at 450°C, because there are some cracking reactions already happened even at 410°C. In fact, the actual reaction time at 450°C is longer than the preset time due to the more heating time, and it is also because of the higher temperature lead to the higher vapor pressure. The results in Table 2 shows that the reaction with higher temperature would produce more gas, especially if T<420°C little gas is produced, so the residual pressure could not read out by the pressure meter. Hence according to the pour point, viscosity, density, and gas production, 420°C should be the best reaction temperature.

![Figure 1. The viscosity and density of the cracked oil at different reaction temperature (30 min). a: the effect of temperature to the viscosity of the product; b: the effect of temperature to the density of the product.](image1)

![Figure 2. The pressures during different reaction times](image2)

| Reaction temperature, °C | 450 | 430 | 420 | 410 |
|--------------------------|-----|-----|-----|-----|
| Residual pressure, psi   | 40  | 20  | 0   | 0   |

3.2. The effect of the different reaction time
Different reaction time from 30 minutes to 5 minutes was investigated, and the pour point test results of the cracked oil are given in Table 3. It shows that the cracked oil produced in the 30 minutes and 20 minutes could both pass the pour point tests, but the two products in 10 minutes and 5 minutes couldn’t pass the pour point test, which means the reaction time is not enough. Since the cracked oil produced in 20 minutes could meet the requirement of the pour point test and also save time, 20 minutes should be the suitable reaction time.

| Reaction time, minutes | 30  | 20  | 10  | 5  |
|------------------------|-----|-----|-----|----|
| Passed the pour point or not (at 2°C) | Passed | Passed | Not passed | Not passed |

The results in Figure 3 show the effect of different reaction time on the viscosity and density. With longer reaction time, the viscosities and densities decrease especially between 20 minutes and 30 minutes, but since the pour point of the product by 20 minutes already far exceed the requirement, thus 20 minutes is enough, the viscosity is 2.63 mP•s, and the density is 0.784 g/cm³.

![Figure 3](image.png)

**Figure 3.** The viscosity and density of the cracked oil in different reaction time (420°C). a: the effect of temperature to the viscosity of the product; b: the effect of temperature to the density of the product.

The pressures before and after the reaction at 420°C with different reaction time are described in Figure 2. It shows that the reaction the pressures read 80psi, 100psi, 120psi and 140psi after 5 minutes, 10 minutes, 20 minutes and 30 minutes, which means the more reaction time the more gas produced, so the pressure increase accordingly. The residual pressures are also recorded in Table 4. It indicate that there is no read at room temperature during the investigated reaction time from 30 minutes to 5 minutes which illustrate little gas produced, but it doesn’t mean there is completely no gas produced. When opening the gas outlet valve of the reactor, there was some gas coming out.

| Reaction time, minutes | 30  | 20  | 10  | 5  |
|------------------------|-----|-----|-----|----|
| Residual pressure, psi  | 0   | 0   | 0   | 0  |

### 3.3. Analysis of the final product

To make sure the compound difference before and after the cracking reaction, FTIR was used to check the product(B) produced at 420°C with 20 minutes to compare with the raw waxes(A). The results are demonstrated in Figure 4.
Figure 4. The FT-IR spectra of the waxes before (A) and after (B) the thermal cracking.

In Figure 4, the 2955 and 1377 cm\(^{-1}\) are associated with -CH\(_3\) [9], [10], and 2850-2921 cm\(^{-1}\) are corresponded to symmetric and asymmetric stretching frequency –CH\(_2\) [11]-[13]; 1463 cm\(^{-1}\) indicate CH\(_2\)- bending [12], [14], 720 cm\(^{-1}\) is due to the deformation vibration in (-CH\(_2\)-)\(_n\) groups [15], both 887.59 and 964.96 cm\(^{-1}\) show -CH=CH\(_2\) functional groups [16], 909.06 cm\(^{-1}\) indicate -CH=CH- newly produced [17]. Why the double bond hydrocarbons are produced in the cracked oil also prove the thermal cracking mechanism as follows.

\[
\text{R-CH-CH}_2\text{-R'→R-CH=CH}_2+\text{R'H} \quad (1)
\]

\[
\text{R-CH}_2\text{-CH}_3\rightarrow\text{R-CH=CH}_2+\text{H}_2 \quad (2)
\]

From the equation (1) and (2), it shows that the thermal cracking reaction typically both the carbon bond breaking and dehydrogenation lead to the unsaturated hydrocarbon newly produced, and from the residue pressure records, it comes to a conclusion that the lower temperature the lighter thermal cracking, so fewer gases are produced. It is known that the carbon bond breaking is easier than the dehydrogenation, and the longer carbon chain the easier rupture, thus to get more short carbon chain hydrocarbon liquids, less gas production and to avoid possible further more secondary cracking for more gases, lower temperature and shorter time should be better, it also support that 420°C and 20 minutes are better parameters but not higher temperature and longer time since the acceptable product has been turned out already.

The FT-IR spectral data is corroborated by the \(^{13}\)C NMR spectrum of the final cracked liquid product in Figure 5, which shows two major functional groups. The peaks from 10 to 40 ppm are assigned to aliphatic hydrocarbon side chains [18], while the peaks from 110-140 ppm are assigned to olefin carbon [19], and the peaks at 77 are assigned to the solvent CDCl\(_3\). Thus on the evidence of the FI-IR and the \(^{13}\)C NMR spectrum, it reaches the conclusion that there are some unsaturated hydrocarbons produced during the cracking reaction, and most of the products are saturated hydrocarbons.
To check if the hydrogen was produced, the gas from the final experiment (420 °C and 20 minutes) was collected and analyzed, the results is recorded in Table 5. It shows that the hydrogen is produced and the volume percentage is 2.96%, which proves the dehydrogenation equation (1) above. The percentage of the hydrocarbon from methane to pentane achieves at 28.43% and far more than the volume of the hydrogen, which also indicate that the carbon bond breaking is easier than the dehydrogenation under the same condition, so it is helpful to produce more saturated hydrocarbons and less olefins.

Table 5. The gas components from the final product

| Gas content | H<sub>2</sub> | CH<sub>4</sub> | C<sub>2</sub>H<sub>4</sub> | C<sub>3</sub>H<sub>6</sub> | C<sub>4</sub>H<sub>6</sub> | C<sub>4</sub>H<sub>8</sub> | C<sub>4</sub>H<sub>10</sub> | C<sub>5</sub>H<sub>10</sub> | C<sub>5</sub>H<sub>12</sub> |
|-------------|------------|-------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Volume percentage, % | 2.96 | 5.13 | 1.83 | 5.74 | 4.48 | 4.99 | 2.04 | 2.65 | 0.77 | 0.80 |

To compare the heating value difference and the elemental composition variation before and after the thermal cracking, the HHV and elemental analysis of the wax and final liquid product are recorded in Table 6. It shows that the carbon content in final liquid product is higher than the wax; the hydrogen in final product is less than the wax, which is due to the dehydrogenation of the thermal reaction. As to the nitrogen there are just 0.01% differences between the wax and final liquid product, maybe it is because of the nitrogen flash of the reactor. There is no sulfur and oxygen in wax and final liquid product. The HHV of the final liquid product is lower than the wax because the dehydrogenation reaction leads to some hydrogen loss, whose heating value is higher than carbon. Although there is about 0.56 MJ/kg higher heating value losses of the final liquid product as compared to the wax, the liquid product is more convenient to be transported or utilized. What’s more, the gas product could be also used as fuels.

Table 6. The EA and HHV of the final liquid product

| Elemental composition (Wt%) | Wax | Final liquid product |
|-----------------------------|-----|----------------------|
| C                           | 84.87 | 85.07                |
| H                           | 14.31 | 14.10                |
| N                           | 0.82  | 0.83                 |

Figure 5. The 13C NMR spectrum of the final liquid product
4. Conclusion
Moderate thermal cracking was used to investigate the soft waxes processing, and the properly reaction parameters were selected out. The FT-IR analyzing of the oil product proved that the unsaturated hydrocarbons newly appeared which was corroborated by the $^{13}$C NMR spectrum. The GC analyzing showed that the hydrogen was produced, it meant the dehydrogenation reaction happened which was also proved by the elemental analysis and HHV results. The original paste waxes were converted into hydrocarbon liquids; the pour point of the final product far more achieved the required target of the factory. So non-catalytic thermal cracking to deal with the soft waxes is a convenient and cheap way to get liquid products.

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