

Article

Analysis of the Composition and Thermogravimetric Kinetics of Vacuum Residue from Karamay

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Abstract

Vacuum residue (VR) is one of the more difficult heavy fractions to process in petroleum refining, and the development of clean utilization technologies for vacuum residue has become a major research focus in the petrochemical industry. This paper discusses the compositional and structural characteristics of vacuum residue from Karamay (KVR) using methods such as ultimate analysis, FTIR, and TG-DTG. The thermal gravimetric kinetics analysis was conducted based on TG-DTG curves at different heating rates. Ultimate analysis revealed that KVR has a high H/C atomic ratio (1.84), and combined with the strong peaks at 2920 cm^{-1} and 2850 cm^{-1} in its infrared spectrum, it indicates that KVR is mainly composed of aliphatic compounds, with aromatic compounds being relatively few. High-temperature simulated distillation showed that KVR had a broad boiling-range distribution, with the temperature corresponding to a cumulative recovery of 86.4% exceeding $720\text{ }^{\circ}\text{C}$, indicating the presence of a certain proportion of ultra-high-boiling components in KVR. The Coats–Redfern kinetic model shows significant variations in activation energy (E_a) at different temperature ranges and reaction orders. Kinetic studies using non-model methods show smaller differences in E_a derived from four different non-model methods. Overall, KVR's pyrolysis process is complex, with E_a ranging between 100 and 300 kJ/mol .

Keywords: vacuum residue; composition and structure; boiling-point distribution; TG-DTG; thermogravimetric kinetics



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1. Introduction

Petroleum is the primary resource on which modern industry relies, while vacuum residue (VR) is a heavy fraction in the petroleum refining process that is difficult to process. Its heavy characteristics, such as high viscosity and high metal content, pose significant technical and investment challenges for direct processing [1–3]. Historically, the utilization of VR has mainly focused on producing low-value fuels and construction asphalt [4,5].

Driven by the global low-carbon transition and China's "Carbon Peak and Carbon Neutrality" strategy goals, the high-value utilization and clean processing technologies of VR have emerged as a current research focus in the petrochemical field [6–9].

Common high-value processing technologies for VR include catalytic hydrocracking, in which VR reacts with H_2 under the action of a catalyst to remove impurities, lighten the fraction, and improve its properties, converting low-quality VR into more valuable light-oil products (such as diesel and naphtha) [10–12]. Golmohammadi et al. [13] synthesized CeO_2 , Co_3O_4 , and MnO_2 nanoparticles via a supercritical water method and evaluated their catalytic performance and stability during the supercritical water cracking of vacuum residue (VR) at 450 °C for 60 min. Their results demonstrated that all three nanocatalysts promoted the conversion of asphaltenes into lighter fractions while suppressing coke formation. The catalytic activity followed the order of $CeO_2 > Co_3O_4 > MnO_2$. Among them, CeO_2 exhibited the highest catalytic activity and superior phase stability during the reaction. However, its catalytic performance gradually declined upon repeated use due to particle agglomeration and the associated reduction in specific surface area. However, during the catalytic hydrocracking of VR, asphaltenes tend to precipitate, causing fouling in equipment and pipelines that limits long-term stable operation of the unit, while also poisoning the catalyst and reducing hydrocracking efficiency [13–16].

On the other hand, the hydrogenation of VR is accompanied by the thermal weight-loss behavior of VR, which can lead to equipment fouling and catalyst poisoning. The hydrogenation of residue oil is accompanied by thermal weight loss, which can lead to equipment coking and catalyst deactivation. Carbognani et al. [17] investigated the boiling-range distributions of vacuum residue and its visbreaking products using high-temperature simulated distillation (HTSD). They found that the high-temperature chromatographic peaks were mainly associated with heavy resins and asphaltenes, and that their peak areas decreased with increasing cracking severity. Kaminski [18] compared the thermal cracking behaviors of Arabian atmospheric residue (AR) and vacuum residue (VR). Compared with VR, thermal cracking of AR produced a higher liquid yield and API gravity, together with lower gas and coke yields, indicating that direct upgrading of AR is advantageous for reducing coke formation and increasing light-oil yield. Wang et al. [19] investigated free-radical generation and coke formation during the cracking of two vacuum residues and their saturate, aromatic, resin, and asphaltene (SARA) fractions. They found that coke formation involved the aggregation of asphaltene macromolecules during the early stage of cracking, indicating that asphaltene structure and free-radical condensation play important roles in controlling coke formation during VR cracking. Park [20] investigated the non-isothermal pyrolysis behavior of vacuum residue under a nitrogen atmosphere using thermogravimetric analysis at heating rates of 2, 5, 10, and 20 °C/min, and analyzed the reaction process using kinetic models. The results showed that the temperature corresponding to the maximum pyrolysis rate shifted to higher values with increasing heating rate.

To investigate the thermal cracking behavior of vacuum residue (VR) under non-catalytic conditions, Karamay vacuum residue (KVR) was characterized by ultimate analysis, Fourier-transform infrared spectroscopy, TG–DTG analysis, and high-temperature simulated distillation. The thermal cracking process and kinetic parameters were further analyzed using the Coats–Redfern model-fitting method and model-free kinetic methods. The results provide a basis for understanding the thermal stability and cracking reactivity of vacuum residues, thereby supporting the optimization of vacuum distillation and thermal cracking processes.

2. Materials and Methods

2.1. Sample

The sample was obtained from the vacuum residue of a petrochemical company in Karamay (KVR), which is a heavy fraction derived from crude oil after vacuum distillation. The production of vacuum residue generally involves the following two steps. First, crude oil distillation is carried out near atmospheric pressure to separate light petroleum products such as liquefied gas, gasoline, and diesel. Then, vacuum distillation is performed, in which the bottom fraction from the crude oil distillation column is further heated and separated under reduced pressure, resulting in vacuum residue.

2.2. Main Analytical Methods

(1) Ultimate Analysis

The ultimate elemental composition of KVR was analyzed using a Vario EL III elemental analyzer, including C, H, N, and S contents. The atomic H/C ratio was subsequently calculated.

(2) Functional Group Analysis

FTIR analysis was performed using a Bruker TENSOR 27 spectrometer (Bruker Corporation, Billerica, MA, USA). The sample was mixed with KBr at a mass ratio of 1:20, ground, and pressed into a pellet. Measurements were conducted in the scanning range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans per sample.

(3) High-Temperature Simulated Distillation

The boiling point distribution of KVR was determined using a SimDis HT analyzer (Analytical Controls by PAC, Rotterdam, The Netherlands) in accordance with ASTM D7169.

(4) Thermogravimetric Analysis

Thermogravimetric analysis was carried out using an SDT-Q600 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA). About 5–10 mg of KVR was weighed and heated from room temperature to 1000 °C at heating rates of 5, 10, 15, and 20 °C·min^{−1} under a N₂ flow of 100 mL·min^{−1}.

2.3. Kinetic Models and Methods

2.3.1. Model-Based Method

The most commonly used model-based method is the Coats–Redfern model. By selecting an appropriate kinetic function $g(\alpha)$, the activation energy E_a can be calculated using a single heating rate. The Coats–Redfern model is expressed as follows:

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\beta E_a} - \frac{E_a}{RT}. \quad (1)$$

where $g(\alpha)$, α , T , A , R , β , and E_a represent the kinetic function, combustion conversion, absolute temperature, pre-exponential factor, universal gas constant (0.008314 kJ·mol^{−1}·K^{−1}), heating rate, and activation energy, respectively.

2.3.2. Model-Free Method

The model-free method refers to obtaining more accurate kinetic parameters at constant conversion rates. This approach avoids the need to select a kinetic function $g(\alpha)$, thereby providing a more precise determination of the activation energy (E_a). Common model-free methods include the Ozawa [21], KAS [22], Friedman [23], and Starink [21] approaches.

(1) Ozawa Method

$$\ln(\beta) = \ln \left[\frac{AE}{Rg(x)} \right] - 5.331 - 1.052 \frac{E}{RT} \quad (2)$$

(2) KAS Method

$$\ln\left(\frac{\beta}{T^2}\right) = \ln \left[\frac{AE}{Rg(x)} \right] - \frac{E}{RT} \quad (3)$$

(3) Starink Method

$$\ln\left(\frac{\beta}{T^{1.8}}\right) = \ln \left[\frac{AE}{Rg(x)} \right] - 1.0037 \frac{E}{RT} \quad (4)$$

(4) Friedman Method

$$\ln\left(\frac{dx}{dt}\right) = \ln(Af(x)^n) - \frac{E}{RT} \quad (5)$$

3. Results and Discussion

3.1. Ultimate Analysis

Ultimate analysis indicates that KVR is primarily composed of carbon and hydrogen, with carbon accounting for 78.76%, hydrogen 12.07%, and nitrogen 0.29%, resulting in an H/C ratio of 1.84 (Table 1). This H/C ratio is relatively high compared to other VRs (e.g., 1.36 reported in [8]), suggesting that KVR contains a higher proportion of aliphatic compounds and fewer aromatic compounds.

Table 1. Ultimate analysis of KVR (wt.%).

Sample	C _{daf}	H _{daf}	N _{daf}	S _{daf}	O *	H/C
KVR	78.76	12.07	0.29	0.38	8.50	1.84
JPVR [8]	84.29	9.537	0.73	3.56	1.883	1.36

daf: dry ash free base; *: by difference subtraction calculation.

3.2. Functional Group Characteristics

3.2.1. Distribution of Functional Groups

The FTIR spectrum of KVR is shown in Figure 1. Strong absorption peaks are observed at 2920 cm^{−1} and 2850 cm^{−1}, corresponding to the asymmetric and symmetric stretching vibrations of aliphatic -CH₂- groups, indicating a high content of aliphatic compounds in KVR [16]. The stretching vibration of the >C=C< framework in aromatic rings appears around 1591 cm^{−1} [24], suggesting the presence of aromatic structures in KVR. The symmetric bending vibrations of -CH₂- and -CH₃ groups are observed near 1452 cm^{−1} and 1372 cm^{−1}, respectively, with the -CH₂- peak showing a higher intensity. A weak absorption peak at 1028 cm^{−1} is attributed to the S=O stretching vibration [25], indicating the presence of sulfur-containing compounds in KVR at relatively low levels, which is consistent with the ultimate analysis results. Absorption peaks in the range of 900–700 cm^{−1} correspond to out-of-plane bending vibrations of C-H bonds at different substituted positions on the aromatic rings.

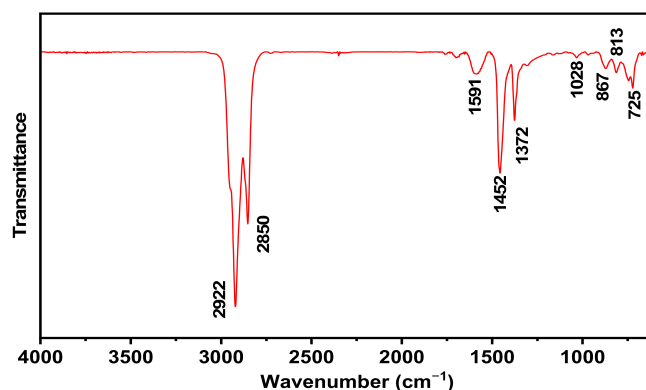


Figure 1. Infrared spectrum of KVR.

3.2.2. FTIR Semiquantitative Analysis

To further investigate the molecular structural features of KVR, PeakFit v4.12 software was used to perform peak semiquantitative analysis in three spectral regions: 2800–3000 cm^{-1} , 1000–1800 cm^{-1} , and 700–900 cm^{-1} . The results are shown in Figure 2, and the functional group assignments and relative peak areas of the sub-peaks are summarized in Table 2.

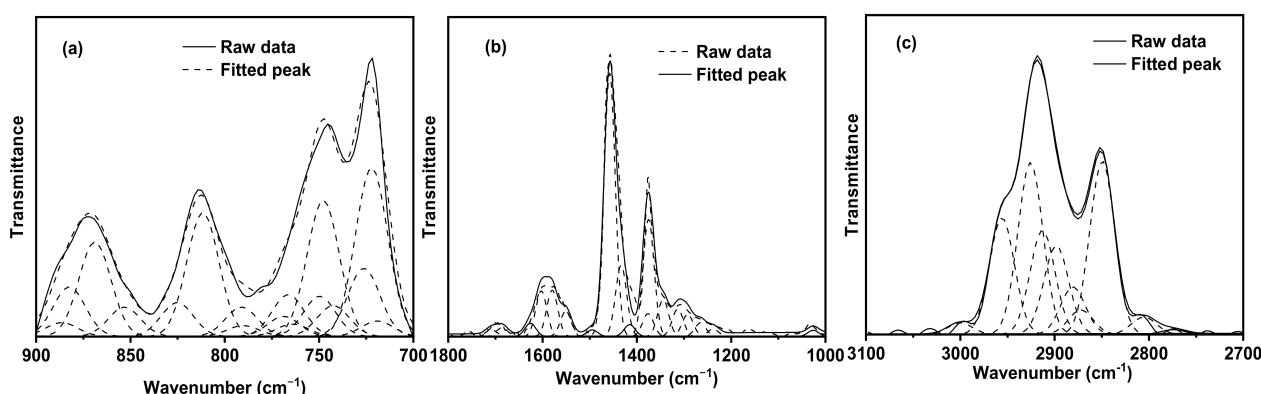


Figure 2. FT-IR curve fitting of KVR in different wavenumber regions: (a) 900–700 cm^{-1} ; (b) 1800–1000 cm^{-1} ; (c) 3100–2700 cm^{-1} .

Table 2. Mole fraction of functional groups for KVR.

Wavenumber (cm^{-1})	Functional Group Structure	Content (Area %)
2960–2955	$-\text{CH}_3$ asymmetric stretching vibration	21.17
2928–2925	$>\text{CH}_2$ asymmetric stretching vibration	31.20
2894–2890	Aliphatic $>\text{CH}$ stretching vibration	16.16
2853–2850	Aliphatic $>\text{CH}_2$ symmetric stretching vibration	31.47
1658–1655	Carboxylic acid $>\text{C}=\text{O}$	0
1608–1605	Conjugated $>\text{C}=\text{O}$	10.24
1573–1570	Aromatic ring $\text{C}=\text{C}$ stretching vibration	12.26
1516–1510	$-\text{CH}_3$ and $>\text{CH}_2$ asymmetric bending vibration	0
1455–1450	CH_3 -Ar, R vibrations	24.38
1375–1370	$-\text{CH}_3$ symmetric bending vibration	38.52
1317–1315	Carboxyl $\text{C}-\text{O}$	8.06
1263–1260	Ester $\text{C}-\text{O}$ stretching vibration	6.55
1204–1200	Alkyl ether	0
865–860	Out-of-plane vibration of $=\text{CH}$ on aromatic ring (5 H)	29.64
810–805	Out-of-plane vibration of $=\text{CH}$ on aromatic ring (4 H)	49.86
760–755	Out-of-plane vibration of $=\text{CH}$ on aromatic ring (3 H)	20.50
732–730	Out-of-plane vibration of $=\text{CH}$ on aromatic ring (2 H)	0

As shown in Table 2 for the 2800–3000 cm^{-1} region, KVR is mainly composed of asymmetric and symmetric stretching vibrations of $>\text{CH}_2$ groups. This indicates that KVR contains a significant amount of long-chain alkanes, which also explains its relatively high H/C ratio.

In the 1000–1800 cm^{-1} region, KVR is mainly composed of $-\text{CH}_3$ structures, and the oxygen-containing functional groups are primarily $>\text{C}=\text{O}$. In general, the oxygenated compounds in KVR are mainly carbonyl- or ketone-type compounds.

In the 700–900 cm^{-1} region, it can be observed that KVR also contains a small amount of aromatic compounds.

No absorption peaks were detected in the 3100–3600 cm^{-1} region, indicating that hydroxyl groups are almost absent in this sample.

3.3. Boiling Point Distribution of KVR

Figure 3 presents the results of high-temperature simulated distillation. KVR exhibits a broad boiling-range distribution, with an initial boiling point of 355.5 °C. The temperature corresponding to a cumulative recovery of 86.4% exceeds 720 °C, indicating that KVR still contains a certain proportion of ultra-high-boiling components. These components mainly include high-molecular-weight saturated and long-chain hydrocarbons, highly condensed polycyclic aromatic structures, resins, asphaltenes, high-molecular-weight heteroatom-containing heavy compounds, and metal-containing heavy organic species. The presence of these ultra-high-boiling components contributes to the increased viscosity of KVR and reduces its thermal stability, thereby enhancing its tendency toward coke formation.

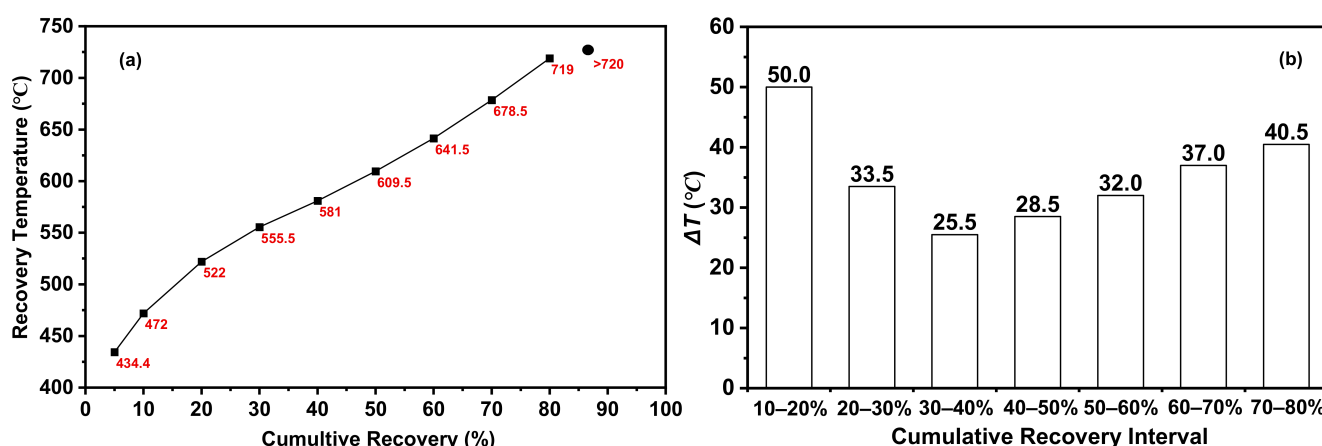


Figure 3. (a) High-Temperature Simulated Distillation Curve; (b) Boiling Range Width Across Recovery Intervals.

In contrast, more than 80% of the components in KVR have simulated boiling points below 720 °C. This result suggests that, after removal of the ultra-high-boiling fraction, fractions with different boiling ranges and molecular-weight distributions could potentially be recovered through controlled-temperature separation. As shown in Figure 3b, an increase of 25.5–50 °C is required for each additional 10% cumulative recovery.

3.4. Thermogravimetric Behavior and Kinetic Analysis

3.4.1. Thermogravimetric Curves

The TG-DTG curves of KVR at different heating rates are shown in Figure 4. Based on the TG-DTG data, the characteristic parameters of the weight-loss process are listed in Table 3. As shown in Figure 4, the weight-loss trends of KVR are consistent at different heating rates, with weight losses exceeding 90%, indicating a high degree of volatilization, evaporation, and cracking. Generally, the residual mass after weight loss represents the coke

formed by the polycondensation of asphaltenes during the pyrolysis of KVR [16]. From 30 to 300 °C, KVR exhibits minimal weight loss, reflecting its good thermal stability. The weight loss in this stage mainly results from the release of small molecules due to surface adsorption or slight cracking [22]. The main weight-loss stage occurs between 300 °C and 500 °C, which primarily involves thermal conversion of KVR based on radical reaction mechanisms, including side-chain cleavage of cycloalkanes and aromatics, dehydrogenation and ring-opening of cycloalkanes, dehydrogenation and condensation of aromatics, and cleavage of C-C and C-H bonds in hydrocarbons as well as bonds between carbon and heteroatoms (e.g., S and N) in non-hydrocarbon species [26]. From the DTG curves, it can be seen that only a single weight-loss rate peak appears at each heating rate, indicating that the pyrolysis of KVR is relatively concentrated and predominantly occurs within 300–500 °C. Notably, the TG curve obtained at a heating rate of 10 °C·min^{−1} differed from those obtained at the other three heating rates, showing a markedly higher coke residue in the final stage. This may indicate that an appropriate heating rate favors coke formation.

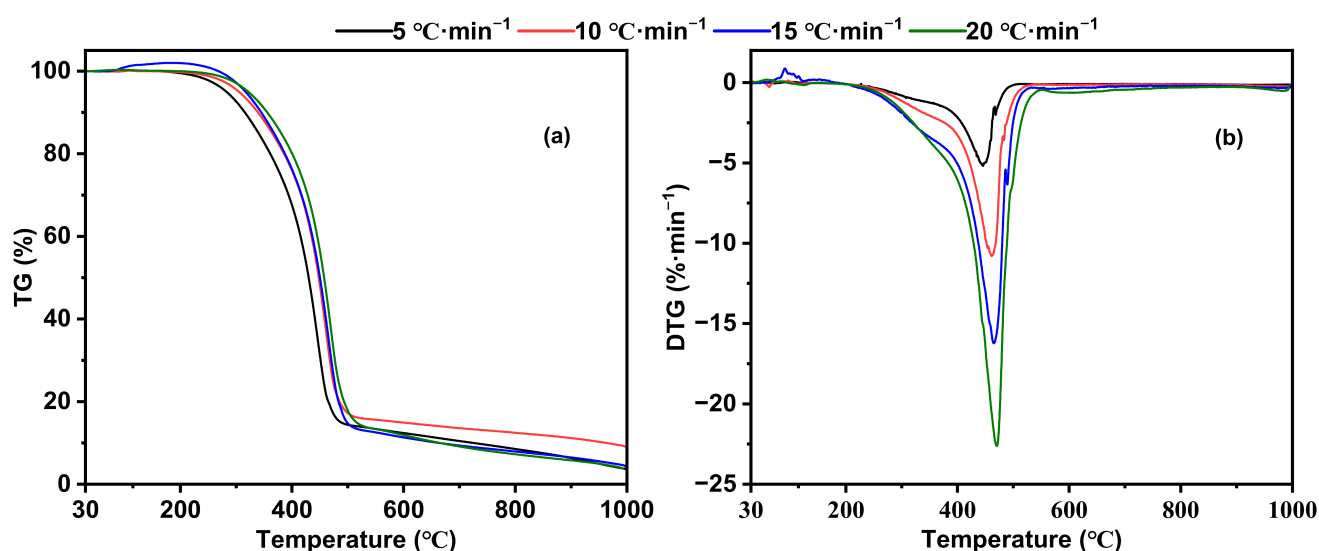


Figure 4. TG (a) and DTG (b) curves of KVR.

Table 3. Effect of heating rate on pyrolysis characteristics of vacuum residue oil.

Heating Rate (°C·min ^{−1})	T_i (°C)	T_{max} (°C)	T_f (°C)	$(dw/dT)_{max}$ (%·min ^{−1})
5	175.6	445.8	489.3	−5.2
10	232.1	461.2	505.3	−10.8
15	251.9	465.1	508.0	−16.2
20	264.3	470.3	529.3	−22.6

T_i : initial decomposition temperature; T_{max} : temperature at maximum weight loss rate; T_f : final decomposition temperature; $(dw/dT)_{max}$: maximum weight loss rate.

As shown in Figure 4 and Table 3, with increasing heating rates (5–20 K·min^{−1}), the initial temperature of weight loss gradually increases, and both the peak intensity of the maximum weight-loss rate and the final pyrolysis temperature also rise. This behavior is mainly attributed to heat transfer limitations and thermal lag [27], which cause a larger temperature difference between the sample and the furnace. The maximum weight-loss rate generally increases with increasing heating rate.

3.4.2. Macroscopic Kinetic Modeling Based on the Coats–Redfern Model

To further investigate the macroscopic reaction characteristics during the pyrolysis of KVR, the Coats–Redfern kinetic model was employed. A single heating rate (10 °C·min^{−1})

was selected, and kinetic fitting was performed under different reaction orders ($n = 1-4$). The results are presented in Table 4. It can be seen that the activation energy (E_a) varies significantly across different temperature ranges and reaction orders. For all three temperature ranges, the goodness of fit slightly decreases with increasing reaction order (based on R^2), with particularly low fit quality observed in the 683–735 K range.

This discrepancy is due to the complex and variable nature of KVR pyrolysis, which involves melting, volatilization of light fractions, and cleavage of long-chain alkanes during the heating process. Therefore, using a single reaction model to describe the entire thermogravimetric process is inaccurate and leads to significant deviations.

Table 4. Calculated values of Coats–Redfern pyrolysis kinetic parameters for KVR.

Temperature Range (K)	Reaction Order	Regression Equation	R^2	E_a (kJ/mol)
607–683	1	$y = -5.25x - 6.41$	0.999	43.65
	2	$y = -5.93x - 5.23$	0.999	49.30
	3	$y = -6.67x - 3.98$	0.998	55.45
	4	$y = -7.45x - 2.65$	0.997	61.94
683–735	1	$y = -10.16x - 0.72$	0.983	84.47
	2	$y = -14.37x - 7.00$	0.969	119.47
	3	$y = -19.40x + 14.49$	0.956	161.29
	4	$y = -25.13x + 23.00$	0.946	208.93
735–744	1	$y = -16.24x + 9.08$	0.999	135.02
	2	$y = -31.43x + 30.41$	0.999	261.31
	3	$y = -51.30x + 58.23$	0.999	426.51
	4	$y = -73.99x + 89.96$	0.998	615.15

3.4.3. Model-Free Kinetic Analysis of KVR

To further investigate the E_a of KVR at different conversion rates, four model-free kinetic methods—Ozawa, KAS, Friedman, and Starink—were used to fit the pyrolysis process of KVR. The relationships between temperature and pyrolysis conversion at different heating rates are shown in Figure 5a,b.

As shown in Figure 5a, with increasing heating rates, the pyrolysis temperatures corresponding to the same conversion rate exhibit significant thermal lag, which is consistent with the trends observed in the TG curves. Based on the conversion–temperature data ($\alpha = 0.1-0.9$) at different heating rates, fitting was performed using OriginPro 2025 software, and the results are presented in Figure 5c–f. The E_a calculated from different model-free methods are listed in Table 4. In fact, the variation of E_a with conversion (α) reflects the complex chemical reactions occurring during the devolatilization of the sample, including multi-step reactions taking place within the material [22,23].

As shown in Table 4, the fitting correlation coefficients for the four model-free kinetic methods—Ozawa, KAS, Friedman, and Starink—are all high ($R^2 > 0.99$). With increasing pyrolysis conversion, the apparent E_a increases rapidly in the range of $\alpha = 0.1-0.7$ and slightly decreases in the range of $\alpha = 0.7-0.9$. The apparent E_a calculated by the Ozawa, KAS, and Starink methods are relatively close, whereas the Friedman method yields slightly higher E_a values. Overall, the E_a values calculated by the four methods are comparable, ranging from 177 to 200 kJ·mol^{−1}. This differs significantly from the results obtained using the Coats–Redfern method at different reaction orders, indicating certain limitations in the Coats–Redfern approach. This is partly due to the complex composition of KVR, making $g(\alpha)$ a variable function at different temperatures, and partly because the selection of $g(\alpha)$ may not be accurate.

To verify the reliability of the E_a values obtained from the four model-free methods at constant conversion, Equation (2) of the Coats–Redfern model was transformed into Equation (6):

$$E_a = RT \ln \frac{T^2 R}{\beta E_a} - RT \ln \frac{g(\alpha)}{A}. \quad (6)$$

By substituting the E_a expressions obtained from the KAS method at different conversion rates into Equation (6), a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ was selected. Since the same sample was used, the function $g(\alpha)$ is identical at the same conversion rate. Assuming that the pre-exponential factor A is also constant at the same conversion rate, the term $\ln \frac{g(\alpha)}{A}$ remains constant, allowing the calculation of $\ln \frac{g(\alpha)}{A}$.

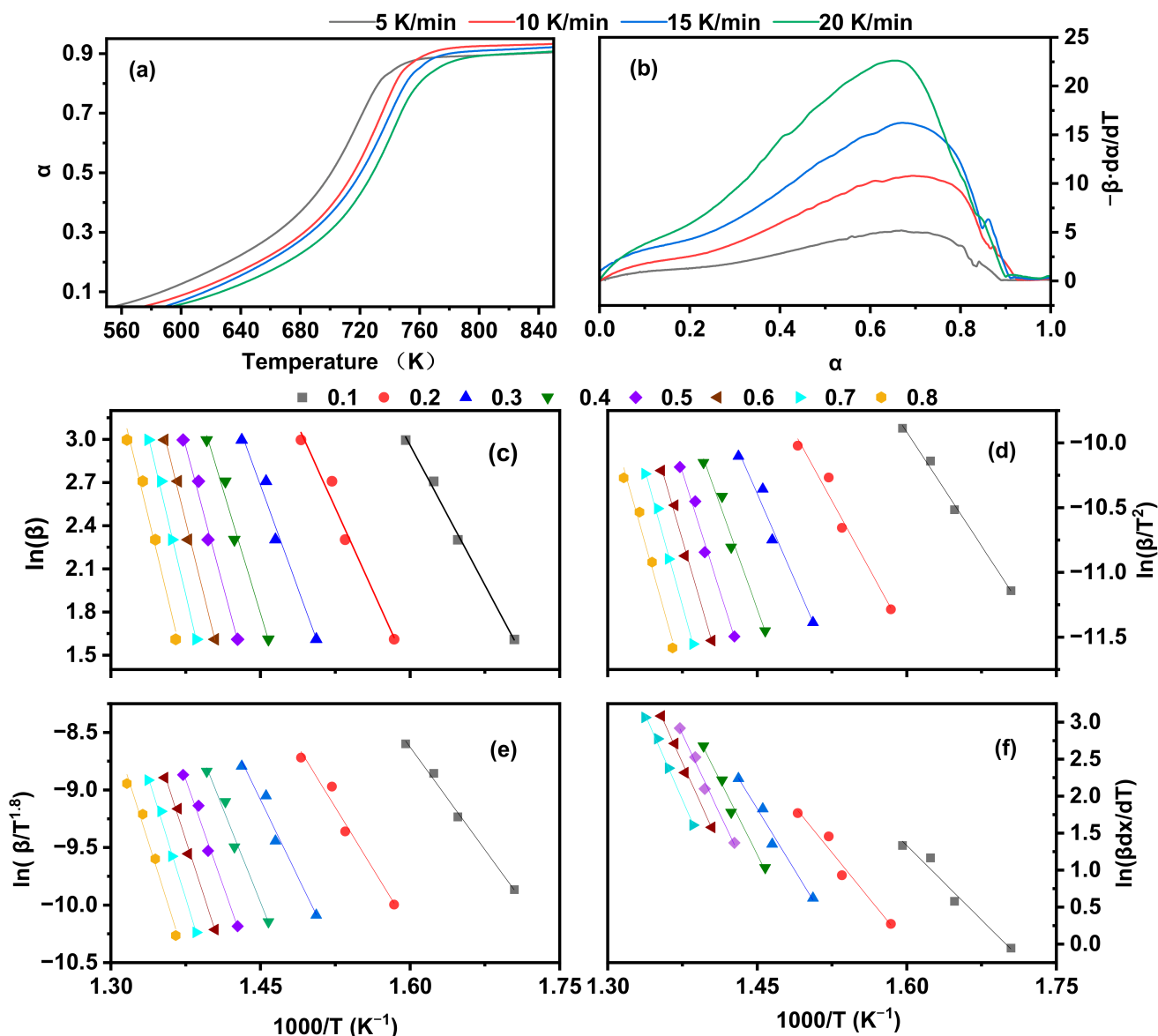


Figure 5. Under different heating rates: (a) relationship between temperature and conversion; (b) relationship between temperature and conversion; Arrhenius fitting curves of KVR: (c) Ozawa method; (d) KAS method; (e) Friedman method; (f) Starink method.

Substituting $\ln \frac{g(\alpha)}{A}$ into Equation (6) for different heating rates and performing iterative calculations, the $E_{a\beta}$ under varying heating rates can be determined. The results are presented in Table 5.

Table 5. Kinetic parameters calculated for KVR by Ozawa, KAS, Starink and Friedman methods.

α	Ozawa		KAS		Starink		Friedman	
	Ea (kJ·mol ^{−1})	R ²	Ea (kJ·mol ^{−1})	R ²	Ea (kJ·mol ^{−1})	R ²	Ea (kJ·mol ^{−1})	R ²
0.1	102.50	0.99	97.76	0.99	98.40	0.99	111.33	0.95
0.2	120.87	0.98	116.34	0.96	116.99	0.96	137.68	0.94
0.3	150.64	0.97	147.16	0.95	147.74	0.96	183.25	0.96
0.4	181.48	0.98	179.28	0.97	179.78	0.97	222.66	0.98
0.5	204.92	0.99	203.71	0.98	204.15	0.98	238.22	0.98
0.6	221.41	0.99	220.87	0.99	221.26	0.99	249.96	0.99
0.7	231.93	0.99	231.79	0.99	232.15	0.99	256.18	0.99
0.8	227.40	0.98	226.82	0.97	227.22	0.97	--	--
0.9	--	−0.43	--	−0.33	--	−0.34	--	--
Mean	180.14		177.97		178.46		199.90	

It can be observed that the difference between $E_{a\beta}$ and the original E_a is minimal, with errors generally below 0.5% and a maximum not exceeding 1%. These results indicate that the activation energy obtained from the four model-free methods is relatively accurate, whereas the Coats–Redfern method, due to the approximation of $g(\alpha)$, may lead to inaccuracies, resulting in unreliable values of E_a (Table 6).

Table 6. Ea and error analysis at different conversion rates.

α	Ea (KVR)	$\ln \frac{g(\alpha)}{A}$	5 K·min ^{−1}		15 K·min ^{−1}		20 K·min ^{−1}	
			Ea ₅	ϵ_5	Ea ₁₅	ϵ_{15}	Ea ₂₀	ϵ_{20}
0.1	97.76	−18.23	97.58	−0.18%	97.31	−0.46%	97.69	−0.07%
0.2	116.34	−20.37	116.05	−0.25%	115.28	−0.91%	116.26	−0.07%
0.3	147.16	−24.96	146.71	−0.31%	145.92	−0.84%	146.91	−0.17%
0.4	179.28	−29.88	178.79	−0.27%	178.16	−0.62%	178.97	−0.17%
0.5	203.71	−33.50	203.26	−0.22%	202.78	−0.46%	203.44	−0.13%
0.6	220.87	−35.91	220.53	−0.15%	220.16	−0.32%	220.69	−0.08%
0.7	231.79	−37.28	231.94	0.06%	231.27	−0.22%	231.80	0.00%
0.8	226.82	−35.97	227.43	0.27%	226.56	−0.11%	227.60	0.34%

Figure 6 shows the relationships between apparent activation energy and conversion obtained from the four model-free methods—Ozawa, KAS, Friedman, and Starink. It can be seen that the trends of activation energy with conversion are almost identical across the different methods. The Friedman method yields slightly higher activation energies compared to the other three methods. Overall, the activation energies range from 100 to 300 kJ·mol^{−1} and generally increase at lower conversions before gradually decreasing at higher conversions.

As shown in Table 4, the average activation energies of KVR calculated by the Coats–Redfern method over the conversion range of 0.10–0.38 were 43.65, 49.30, 55.45, and 61.94 kJ/mol for reaction orders of 1, 2, 3, and 4, respectively. Over the conversion range of 0.38–0.80, the corresponding values increased to 84.47, 119.47, 161.29, and 208.93 kJ/mol. Even at a reaction order of 4, the calculated activation energy did not adequately reproduce the actual activation energy of KVR. This suggests that simple integer-order reaction models are insufficient to describe the complex pyrolysis behavior of KVR, which may involve multiple mechanisms, including multistep reactions, diffusion, nucleation, and interfacial reactions.

These results further indicate that KVR pyrolysis is a multicomponent and multistage process. At low conversion, the process is mainly governed by relatively volatile and readily cracked components, resulting in relatively low apparent activation energies. As conversion

increases, resins, asphaltenes, and condensed aromatic structures become increasingly enriched, accompanied by secondary cracking and coke formation, leading to a substantial increase in the reaction energy barrier. Therefore, a single integer-order Coats–Redfern model cannot adequately describe the overall pyrolysis kinetics of vacuum residue.

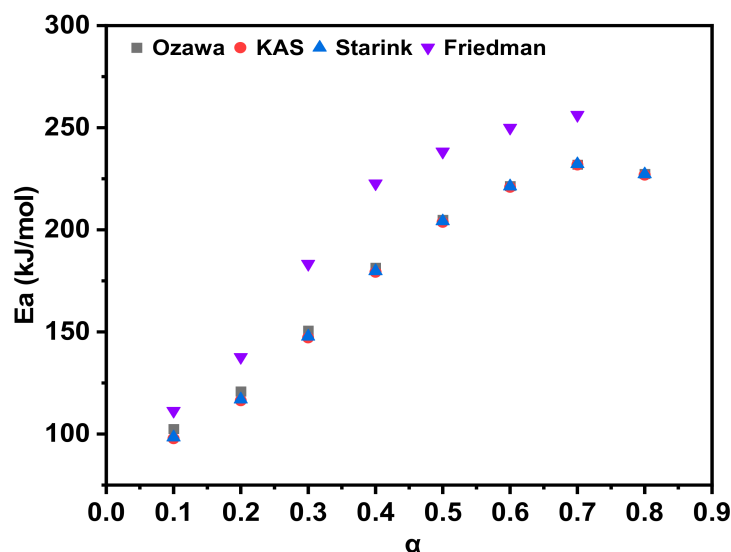


Figure 6. E_a distribution versus α for different methods.

4. Conclusions

This study focused on a vacuum residue from Karamay (KVR) and analyzed its compositional and structural characteristics as well as its pyrolysis behavior. The pyrolysis mechanism was investigated using both model-based and model-free kinetic methods. The main conclusions are as follows:

- (1) Based on ultimate and FTIR analyses, KVR exhibits an H/C ratio of 1.84. Combined with the strong absorption peaks at 2920 cm^{-1} and 2850 cm^{-1} in the FTIR spectrum, this indicates that KVR is primarily composed of aliphatic compounds, while aromatic compounds are relatively scarce.
- (2) High-temperature simulated distillation showed that KVR had a broad boiling-point distribution and contained a certain proportion of ultra-high-boiling components compared with other heavy oils. These components increase the viscosity of KVR, reduce its thermal stability, and promote coke formation.
- (3) The main pyrolysis of KVR occurred at $300\text{--}550\text{ }^{\circ}\text{C}$. The Coats–Redfern method based on a single integer-order reaction model could not adequately describe the overall pyrolysis process of KVR. Model-free methods, including Ozawa, KAS, Friedman, and Starink, gave apparent activation energies ranging from approximately 100 to 300 kJ/mol, which initially increased and then slightly decreased with increasing conversion.
- (4) Based on these results, the low-cost removal of ultra-high-boiling components is considered a key prerequisite for the large-scale utilization of vacuum residue.

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