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Molecular transformation of heavy oil during slurry phase hydrocracking process: Influences of operational conditions

Jing-Man Lu [a, b, 1], Yuan-Feng Wang [a, 1], Zhi-Yuan Zhou [b], Jian-Xun Wu [a], Ya-He Zhang [a], Lin-Zhou Zhang [a, c, **], Quan Shi [a, c, *], Sheng-Bao He [b], Chun-Ming Xu [a]

[a] State Key Laboratory of Heavy Oil Processing, Petroleum Molecular Engineering Center (PMEC), China University of Petroleum, Beijing, 102249, PR China
[b] Petrochemical Research Institute, PetroChina, Beijing, 102200, PR China
[c] CNPC Petrochemical Research Institute and China University of Petroleum Joint Laboratory of Petroleum Molecular Refining, Beijing, 102200, PR China

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ABSTRACT

The influences of reaction temperature, duration, pressure, and catalyst concentration on the molecular transformation of residual slurry phase hydrocracking process were investigated. The molecular composition of the heteroatom compounds in the residue feedstock and its upgrading products were characterized using high-resolution Orbitrap mass spectrometry coupled with multiple ionization methods. The simultaneous promotion of cracking and hydrogenation reactions was observed with increasing of the reaction temperature and time. Specifically, there was a significant increase in the cracking degree of alkyl side chain, while the removal of low-condensation sulfur compounds such as sulfides and benzothiophenes was enhanced. In particular, the cracking reactions were more significantly facilitated by high temperatures, while an appropriately extended reaction time can result in the complete elimination of the aforementioned sulfur compounds with a lower degree of condensation. Under conditions of low hydrogen pressure and catalyst concentration, the products still exhibit a high relative abundance of easily convertible compounds such as sulfoxides, indicating a significant deficiency in the effectiveness of hydrogenation. The hydrogen pressure exhibits an optimal value, beyond which further increments have no effect on the composition and performance of the liquid product but can increase the yield of the liquid product. At significantly high catalyst concentration, the effect of desulfurization and deoxidation slightly diminishes, while the aromatic saturation of highly condensed compounds was notably enhanced. This hydrogenation saturation effect cannot be attained through manipulation of other operational parameters, thereby potentially benefiting subsequent product processing and utilization. This present study demonstrates a profound comprehension of the molecular-level residue slurry phase hydrocracking process, offering not only specific guide for process design and optimization but also valuable fundamental data for constructing reaction models at the molecular level.

Slurry phase hydrocracking process for residual oil typically operates at 400–460 °C and 10–20 MPa (Angeles et al., 2014; Prajapati et al., 2021). In order to improve the conversion effect of residual feedstock and reduce operating costs, large quantities of researches have been conducted on the influence of operating conditions. It was found that increase of reaction temperature and time led to decrease of liquid product and formation of gas and solid products (Martinez-Grimaldo et al., 2014). Although similar residue conversion can be achieved by controlling the reaction temperature and time, the two methods may have different effects on the hydrogenation reaction. For example, when the same conversion is achieved, the coke yield is higher at high temperature for a short time than at low temperature for a long time (Tong et al., 2015). In hence, the ENI slurry technology (EST) uses a long reaction time at low temperature to inhibit the formation of coke. This phenomenon can be better understood by measuring and calculating the dipole moment of the liquid product and the average structure of the asphaltenes therein (Lim et al., 2018). As the reaction temperature was increased, the dipole moment of the liquid product decreased, while the dealkylation of the asphaltenes was aggravated. These two opposite trends resulted in more solid deposition. In contrast, increasing reaction time at low temperature can improve residue conversion with better refining effects because of the better dispersion of the asphaltenes.

Hydrogen pressure and catalyst concentration are also important optimization parameters, which mainly affect the hydrogenation reactions. The removal efficiency of sulfur and Conradson carbon residue (CCR) are highly dependent on the hydrogenation potential of the system, which requires high catalyst concentration and matching high hydrogen pressure. However, the control of coke formation and hydrodemetallization (HDM) can reach ideal effects even at very low catalyst concentration (Panariti et al., 2000). Further research found that under low catalyst concentration, the asphaltenes underwent dealkylation to generate light fractions at low residual conversion, while condensation occurred at high residual conversion to generate coke. Higher catalyst concentration led to a longer coke induction period, asphaltenes were mainly converted to light fractions even at high residual conversion (Nguyen et al., 2021).

In general, the operating conditions have complex influences on the slurry phase hydrocracking process. The prior researches only studied the residual conversion and the bulk properties and average structure of the products, but did not understand the process from molecular composition level, resulting in limited understanding. For example, the conversion reactivity and selectively of a wide variety of compounds in slurry phase hydrocracking process are unknown. By controlling different operating conditions, even if similar conversion rates and product properties are achieved, there may be some differences in the composition of products, which may have impacts on the subsequent processing and utilization of the product. Additionally, since different residual oil feedstocks may have great differences in composition and properties, there may be problems with the applicability of relevant understandings to different feedstocks.

In our recent work (Wang et al., 2023), the molecular composition of a residual oil and its thermal cracking and slurry phase cracking products were obtained using high-resolution mass spectrometry (HR MS). Through the results, the differences in the molecular transformation between slurry phase hydrocracking process and thermal cracking process were clearly reflected, and the mechanism of the reaction process was further discussed. The objective of this work is to track the compositional transformation of residual slurry phase hydrocracking process from a molecular perspective and investigate the influences of operating conditions on it. Four series of slurry phase hydrocracking products of a residual oil feedstock were obtained through changing the reaction temperature, duration, pressure, and catalyst concentration. The molecular composition of the heteroatom compounds in the feedstock and its products was characterized by high-resolution Orbitrap MS coupled with electrospray ionization (ESI) source. The influences of the operating conditions on the hydrocracking process were further discussed via analyzing the bulk properties and molecular composition.

2. Experiment section

2.1. Samples and reagents

The feedstock of the slurry phase experiment is a blend (1:1 *m*/*m*) of a Venezuelan atmospheric residue and a Middle East vacuum residue. The physical properties and composition of the feedstock has been well characterized and reported in a previous work (Wang et al., 2023), and its key bulk properties are listed in Table 1.

Analytical grade *n*-hexane, dichloromethane (DCM), toluene and methanol were obtained from Beijing Chemical Reagents Company, which were purified by distillation with a 9600 spinning band distiller (B/R instrument, USA) before use. Analytical grade silver tetrafluoroborate ($AgBF_4$) and methyl iodide (MeI) were obtained from J&K Chemical Ltd.

2.2. Slurry phase hydrocracking experiments

The slurry phase hydrocracking reactions were carried out in a laboratory-scale batch reactor, and the experimental procedure has been described in a previous publication (Wang et al., 2023). The reactor was continuously fed with H_2 through the gas distributor at the bottom, while its outlet was connected to a condenser to avoid light components being entrained and lost. Oil-soluble molybdenum-containing catalyst was dispersed in the residual oil, which was prepared by the Petrochemical Research Institute, PetroChina. The active component of the catalyst is MoS_2 using ammonium tetrathiomolybdate (ATTM) as precursor (Vasudevan and Zhang, 1994). Following the completion of the reaction, the reactor was completely cooled to room temperature. The resultant liquid in the reactor was carefully collected along with adhering materials present on both the reactor inner wall of the reactor and stirring rods. The liquid products and toluene-insoluble products (or cokes) were obtained through a sequential process of toluene-washing, filtration, and solvent volatilization. The yields of the liquid and coke products were determined through direct weighing, while the remaining mass was calculated as the gas product.

Slurry phase hydrocracking experiments were carried out at different typical operation conditions to investigate their influences on the molecular transformation. A referential experiment was performed under temperature of T °C, duration of t h, pressure of p MPa and catalyst concentration of k wppm. Based on the referential experiment, four series of hydrocracking products were obtained by varying the respective reaction conditions, and the quantitative description of differences in reaction conditions among different products is presented in the subsequent results. Some specific

Table 1
Bulk properties of the feedstock.

Property	Value	Property	Value
ρ^{20}, g·cm^{-3}	0.9848	Ni, μg·g^{-1}	74.8
H/C, mol/mol	1.57	V, μg·g^{-1}	464
S, wt.%	3.78	Asphaltenes, wt.%	9.13
N, wt.%	0.53	Conradson carbon residue, wt.%	13.9

values of the reaction conditions cannot be disclosed due to proprietary information protection.

2.3. Bulk property analysis

The boiling point range of the feedstock and the products was determined by high-temperature simulated distillation analysis according to ASTM D6352-04 method, which was performed using a modified Agilent 6890N GC system (Analytical Controls, Netherland). The GC was equipped with an AC HT-750 (5 m × 0.53 mm × 0.18 μm) high-temperature column. Oven temperature was programed from 40 °C to 430 °C at 10 °C/min with an initial hold time of 1 min and a final hold time of 5 min. The boiling points were calibrated according to the retention times and boiling points of normal alkanes in a standard sample (from n-C_5 to n-C_{120}).

The organic elemental compositions of the feedstock and its hydrocracking products were analyzed by using three instruments employing various methods. The contents of carbon, hydrogen and oxygen were analyzed by a Vario EL Cube elemental analyzer a Rapid OXY Cube elemental analyzer (Elementar, Germany) according to the Chinese standard method GB/T 19143-2017. The contents of nitrogen and sulfur were analyzed by a Multi EA3100 analyzer (Analytik Jena, Germany) according to ASTM D4629-02 and ASTM D5453-1993, respectively.

2.4. Orbitrap MS analysis

The molecular composition of the feedstock and its products was analyzed by HR MS coupled with ESI ionization source. The molecular compositions of non-basic and basic nitrogen compounds in the samples were directly analyzed by the negative-ion and positive-ion modes of the ESI source, respectively. The samples were dissolved in toluene and further diluted with toluene/methanol (1/3, v/v) to 200 mg/L, and then direct injected into the ESI source for analysis. The sulfur compounds were analyzed by methylation derivatization followed by positive-ion ESI analysis, and this ionization method can be called methylation ESI (Müller et al., 2005). The oil samples (approximately 100 mg) were dissolved in 1 mL of DCM and reacted with excess $AgBF_4$ and MeI in the dark for 48 h. A small amount of the supernatant of the methylated product was dipped with a glass capillary, and then dissolved in 1 mL of toluene/methanol (1/3, v/v). The resulting solution was directly injected into the ESI source for analysis.

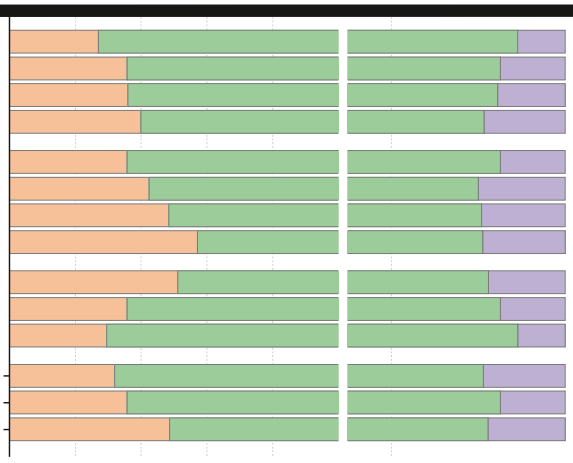
The HR MS analysis was carried out using a Thermo Scientific Orbitrap Fusion mass spectrometer, which exhibited a remarkable mass resolution of 500,000 at m/z 200. The prepared sample solutions were injected directly into the ESI source at 10 μL/min through an injection pump. Spray voltages under positive-ion and negative-ion ESI modes were 3.6 and 2.6 kV, respectively. The sheath, auxiliary, and sweep gas flow rates were set as 5.0, 2.0, 0.1 Arb, respectively. The ion source and the ion transfer tube temperature were 50 and 300 °C, respectively. The ions in the range from m/z 150 to m/z 1000 were recorded in 1 min of detection period. The automatic gain control (AGC) target was set to 500,000, and the maximum injection time was set to 100 ms. The mass spectrum data were exported into a Microsoft Excel file using Thermo Xcalibur software, and subsequently processed with a custom-built program for molecular formula assignment based on the mass values. The principle and details of the data processing have been described elsewhere (Shi et al., 2013).

3. Results and discussion

3.1. Bulk properties of the slurry phase hydrocracking products

The gas, liquid, and coke yields of the slurry phase hydrocracking process are shown in Fig. 1. The liquid yields are all around 90 wt%, which is consistent with liquid yields of typical residual slurry phase hydrocracking processes. The liquid yield is mainly determined by the extent of cracking reaction, which is based on a free radical reaction mechanism (Nguyen et al., 2016). Excessive dealkylation and condensation reactions lead to the generations of gas and coke products, respectively. According to the viewpoint of previous research, MoS_2 catalyst can promote the split of hydrogen to generate hydrogen radicals (Du et al., 2015). High concentration of hydrogen radicals can quench the macromolecule hydrocarbon radicals in the system, thus decreasing the apparent cracking velocity and increasing the liquid yield (Wang et al., 2023). The increase in reaction temperature resulted in a decrease decreased in liquid yield, accompanied by an increase in both gas and coke yields. This phenomenon can be attributed to the promotion of radical reaction initiated at high temperature.

The liquid yield decreased slightly with the increase of reaction duration, while the gas yield increased. It is worthy noticing that the coke yield remained unchanged and even decreased slightly when the reaction duration increased significantly. This represents the condensation reactions tends to be slow in the later stages of the hydrocracking process, while the hydrogenation reactions contribute to the consumption of the coke products. The increase in reaction pressure led to a significant increase in the liquid yield and a decrease in the gas and coke yield, which was caused by the enhanced solubility of hydrogen in the residual oil. As a result, on the one hand, excessive cracking reactions were inhibited, and on the other hand, hydrogenation reactions were promoted. As catalyst concentration increased, the coke yield showed a trend of decreasing, which was caused by the promotion of the hydrogenation reactions. Therefore, although the gas yield increased, the liquid yield only decreased slightly. However, the coke yield increased when the catalyst amount is increased significantly, which is consistent with previous work (Panariti et al., 2000). This trend of increasing coke formation can be explained by the poor



dispersion effect of the high-concentration catalyst. Additionally, the high hydrogenation degree with presence of a large amount of catalyst may lead to stability reduces of asphaltenes, thus promoting the formation of the coke.

Fig. 2 shows the simulation distillation curves of the feedstock and the liquid products. The distillation range can reflect the cracking degree of the hydrocracking process, and the results are consistent with the gas-liquid-coke yield results. The increases of reaction temperature and reaction duration both leads to the increase of the yield of products with low boiling point, indicating that the cracking reactions are promoted. Pressure and catalyst concentration have little effect on the cracking reaction and the resulting distillation range. Appropriate increases of the reaction pressure and catalyst concentration can slightly reduce the cracking degree, resulting in the decrease of the mass yield of low-boiling-point products.

Fig. 3 shows the organic elemental compositions of the feedstock and the liquid products, which can reflect the hydrogenation degree of the reaction process. The content of heteroatoms can reflect the deheteroatom degree, while the H/C ratio can reflect the hydrogenation degree of unsaturated compounds (mainly aromatics). It can be seen that the reaction process has a relatively high removal efficiency on sulfur and oxygen compounds, while the removal efficiency of nitrogen compounds keeps low. The H/C ratios of the products are obviously higher than that of the feedstock. In general, the slurry phase hydrocracking process has a mild hydrogenation effect on the residual feedstock.

With an increase in reaction temperature, the desulfurization rate exhibited a corresponding increase, while the H/C ratio showed an initial rise followed by a subsequent decline. This shows that increasing the reaction temperature at low temperatures mainly promotes the hydrogenation reactions, so that the desulfurization rate and H/C ratio are significantly increased. Increasing the temperature at high temperatures is more conducive to the cracking reactions, which can produce a large amount of small-molecular gaseous hydrocarbons. These gaseous hydrocarbons generally have high H/C ratio, resulting in a slight decrease in the H/C ratio of the liquid product. Increasing the reaction duration has a similar influence on the elemental composition of the liquid product as increasing the reaction temperature. The hydrogenation reaction dominates in the early stage of the reaction, while the hydrogenation reaction tends to slow down and the cracking reaction dominates in the later stage of the reaction. The hydrogenation effect is obviously poor at low hydrogen pressure and catalyst concentration. Further increasing the pressure and catalyst dosage will not significantly improve the hydrogenation effect when appropriate conditions are reached.

3.2. Conversion reactivity of different classes of compounds

The molecular compositions of the feedstock and the liquid products were analyzed through HR MS. HR MS is a powerful tool that can characterize the molecular composition of petroleum

Mass recovery,

especially heavy oil. Different classed of compounds in the feedstock and the liquid products were selectively analyzed through three different ionization methods, and the relative composition of the detected classes of compounds is shown in Fig. 4 (the N1 class refers to the compounds with one nitrogen atom). Due to the characteristics of the ESI source, heteroatom compounds can be selectively ionized, and these compounds are also the most concerned in the residual slurry phase hydrocracking process. Although hydrocarbon compounds are the main compounds in residual oil, heteroatom compounds are also important components and have a decisive impact on the bulk properties. Through the transformation of the composition of these heteroatom compounds, the cracking and hydrogenation performance of the hydrocracking process can be evaluated simultaneously, which is also the main content of the following discussion.

Fig. 4 shows that non-basic N1, basic N1 and S1 are the three primary compound types under the negative-ion ESI, positive-ion ESI, and methylation ESI (methylation derivatization followed by positive-ion ESI) HR MS results, respectively. In the residue feedstock, the poly-heteroatom compounds (e.g., N1O1, N1S1, O1S1 compounds) have high relative abundance. The relative abundance of these compounds decreased obviously in the products after the hydrocracking process. The negative-ion ESI source selectively ionizes compounds with active hydrogen in the samples, including acidic oxygen compounds and non-basic nitrogen compounds (pyrrole compounds). The acidic oxygen compounds in residue feedstock show high relative abundance, including O1 (mainly phenols) and O2 (mainly naphthenic acids) compounds. The naphthenic acids were removed completely during the reaction because of its instability, and the residual acidic oxygen compounds were mainly phenols. Positive ion ESI source mainly ionizes basic nitrogen compounds (pyridine compounds), as well as ketones, esters and sulfoxides. For both non-basic and basic nitrogen compounds, N2 compounds are more difficult to remove than N1 compounds. This is contrary to the denitrogenation selectivity of the hydrotreating process (Zhang et al., 2013; Li et al., 2024), because the hydrogenation activity of the catalyst in the slurry phase hydrocracking process is low. Methylated ESI sources mainly ionize sulfur-containing compounds. The abundance of S2 compounds decreased obviously. This is because the desulfurization activity is relatively high, and S2 compounds can be easily converted to S1 compounds by removing one S atom (Zhao et al., 2021; Chen et al., 2022). The removal efficiency of N1S1 and O1S1 compounds was lower than S1 compounds. In summary, the hydrogenation efficiency of the slurry phase hydrocracking process is not high. The deheteroatom activity of heteroatom compounds in the residue feedstock during slurry phase hydrocracking process can be roughly divided into the following categories: a. Naphthenic acids and sulfoxides, which can be easily removed completely. b. S1 and S2 compounds, the abundance of which is obviously reduced. c. poly-heteroatom compounds. d. N1 and N2 compounds, the conversion rate of which is very low.

Reaction pressure and catalyst concentration have obvious influences on the conversion selectivity of different classes of compounds. At low hydrogen pressure and low catalyst concentration, the relative abundance of compounds with high deheteroatom activity is significantly higher, indicating that the hydrogenation effect is poor. In contrast, reaction temperature and duration have relatively little impact on the hydrogenation effect. It is worth noting that at high catalyst concentrations, the abundance of acidic oxygen compounds increases significantly, which may also be due to the poor dispersion effect of the catalyst.

(c) ESI_Me

3.3. Molecular composition and transformation of main classes of compounds

The compositions of three main classes of compounds (S1, non-basic N1 and basic N1) were further analyzed in order to further clarify the molecular transformation of residue slurry phase hydrocracking process. Fig. 5 shows the double bond equivalent (DBE) versus carbon number plots of the three classes of compounds in the feedstock and the liquid products with different reaction temperatures. For S1 compounds, the compositional differences between the feedstock and the products are obvious, indicating the desulfurization reactions are easy to occur. The relative abundance of sulfides (refer to non-thiophenic sulfur compounds) with low condensation degree (DBE < 6) decreased obviously in the products. The exposed thiophene ring of benzothiophenes (BTs, DBE = 6) were easily hydrogenated during the hydrocracking process (Wang et al., 2023), and dihydro-BTs (2H-BTs, DBE = 5) were detected with high relative abundance in the products. The transformation of the sulfur compounds is sensitive to the reaction temperature. The sulfides were completely removed in the high temperature product, while the relative abundance of BTs and 2H-BTs decreased. High temperature also promoted the cracking of alkyl side chain, resulting in the decrease of average carbon number (C_{wa}).

In contrast, the transformation of nitrogen compounds is not obvious, and the main occurred reactions are the creaking of alkyl side chains and the saturation of aromatic rings. For non-basic N1 compounds, the abundance of carbazoles was significantly increased (DBE = 9), and small quantity of indoles (DBE = 6) were also detected in the products. These compounds are mainly generated by the aromatic saturation of nitrogen compounds with high condensation degree and the further cracking of the generated naphthenic rings. The DBE of basic N1 compounds decreased obviously after the hydrocracking process. A large number of quinoline and pyridine compounds (DBE = 4–7) and amines (DBE < 4) were detected in the products. With the increase of reaction temperature, both of the non-basic and basic nitrogen compounds mainly underwent further cracking of the alkyl side chains without other obvious changes.

Fig. 6 shows the composition of the liquid products with different reaction durations. As the reaction time increases, on the one hand, sulfides and BTs were completely desulfurized, and on the other hand, the cracking degree of all classes of compounds increased. It is worth noting that when the reaction time is (t+1) h and (t+3) h, there is no significant difference in the composition of the liquid product. In hence, an ideal residue conversion effect has been achieved after reaching the appropriate reaction time. With the further increase of reaction time, the reaction rate of all kinds of

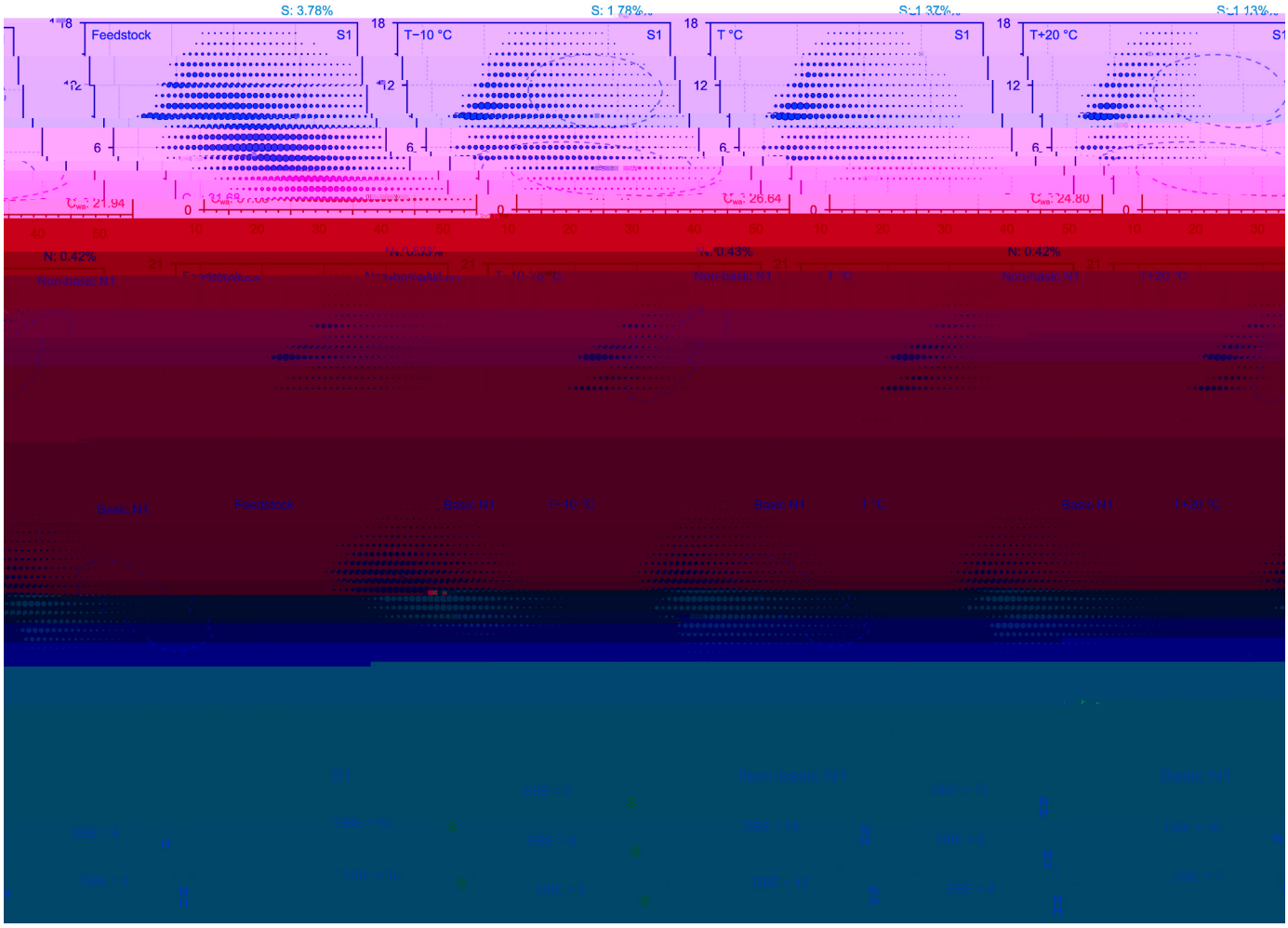
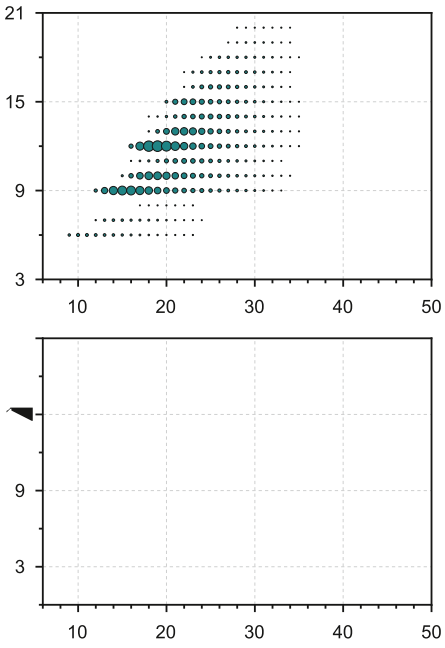


Fig. 5. Ion relative abundance plots of double bond equivalent (DBE) versus carbon number for S1, non-basic N1, and basic N1 class species of the residual feedstock and its hydrocracking liquid products at varying reaction temperatures. The area delineated by the dotted ellipse serves as the reference coordinate for highlighting key regions exhibiting discernible changes in composition. The structures drawn below are proposed positive structures according to the dominant DBE values.



reactions tends to be low. At this time, the effect of desulfurization and cracking is no longer significantly promoted.

Fig. 7 shows the composition of the liquid products with different hydrogen pressures. The effect of deheteroatom is obviously poor and the degree of cracking is high at low hydrogen pressure. The sulfur and nitrogen content of the low-pressure product is high, and a large amount of sulfur compounds with low condensation degree has not been converted. When the reaction pressure is increased, the cracking reactions are inhibited, the desulfurization rate is increased, and the relative abundance of nitrogen compounds with low DBE increased (non-basic N1 compounds with 6~8 DBEs, and basic N1 compounds with 2~5 DBEs). After reaching the appropriate pressure, further increasing the hydrogen pressure has almost no effect on the removal of heteroatoms and the cracking reaction. It can be seen that the compositions of the products under pressures of p MPa and (p+3) MPa are almost the same. However, considering that increasing the hydrogen pressure can effectively increase the liquid yield, the operating pressure can be selected based on technological economics of the process design.

Fig. 8 shows the composition of the liquid products with different catalyst concentration. The influence of the catalyst concentration on the residue conversion effect is similar to that of the hydrogen pressure. The increase of catalyst concentration promoted the hydrogenation reaction and inhibited the cracking reaction, and there was an optimum catalyst concentration. When the catalyst concentration increased from k to 3k wppm, the desulfurization rate decreased and the relative abundance of compounds with high condensation obviously degree decreased (S1 compounds with DBE >12 and basic N1 compounds with DBE >15). This shows that although the high catalyst concentration is not conducive to desulfurization, the aromatic saturation reactions are significantly promoted. This saturation effect cannot be achieved by changing other operating conditions and potentially benefits subsequent product upgrading and utilization processes such as hydrotreating. Additionally, considering that the process may adopt two-step reaction, increasing the catalyst concentration to promote the saturation of aromatics with high condensation degree may be beneficial to their secondary conversion.

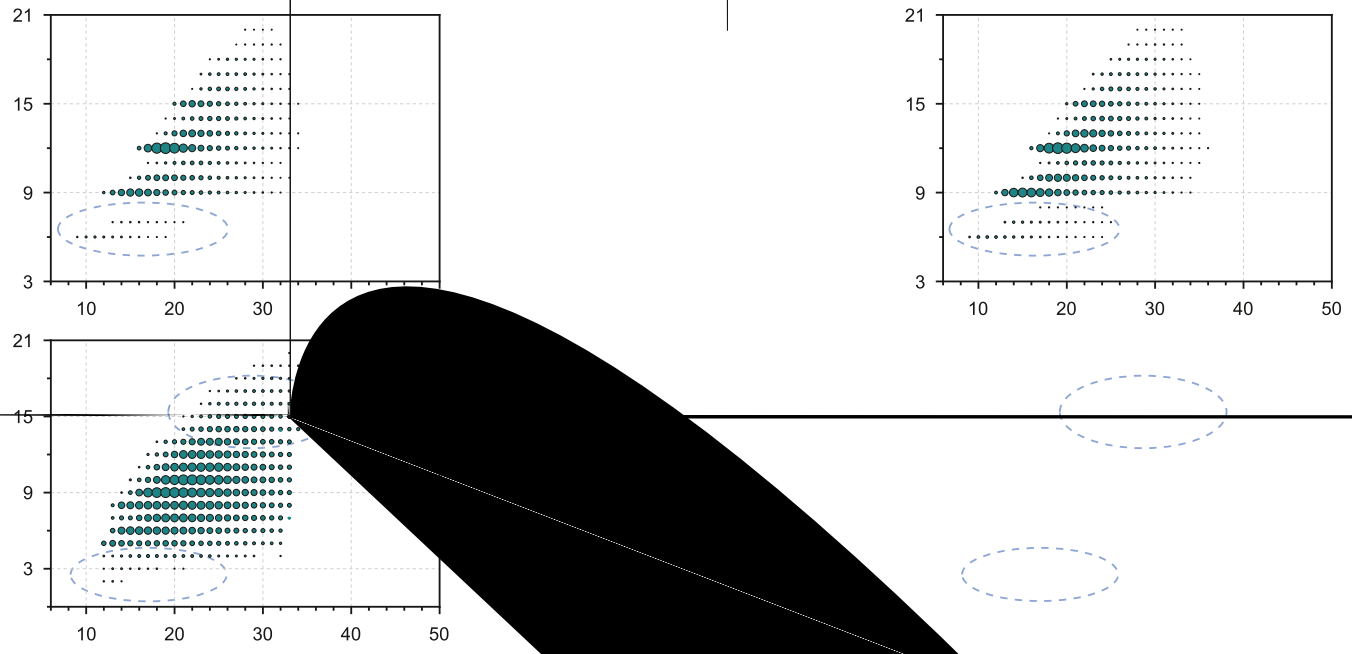
4. Conclusion

By conducting slurry phase hydrocracking experiments on a residual oil under varying reaction temperatures, reaction durations, hydrogen pressures, and catalyst concentrations followed by HR MS analysis, the influences of these operating conditions on the

molecular transformation of the process were systematically investigated. Based on the results, the following conclusions were drawn:

The simultaneous promotion of cracking and hydrogenation reactions was observed with increasing of the reaction temperature and time. Specifically, there was a significant increase in the cracking degree of alkyl side chain, while the removal of low-condensation sulfur compounds such as sulfides and benzothiophenes was enhanced. In particular, the cracking reactions were more easily facilitated by high temperatures, while an appropriately extended reaction time can result in the complete removal of sulfides and benzothiophenes. In the later stage of increasing the reaction durations, both of the cracking and hydrogenation velocities are very low, and the composition and properties of the products no longer change significantly. Therefore, low temperature and appropriately increased reaction time are more beneficial to the residue upgrading.

Hydrogen pressure and catalyst concentration have little effect on the cracking degree, but play an important role in the hydro-



CRediT authorship contribution statement

Jing-Man Lu: Investigation, Data curation, Conceptualization. **Yuan-Feng Wang:** Writing – original draft, Methodology, Investigation, Conceptualization. **Zhi-Yuan Zhou:** Resources, Methodology, Investigation. **Jian-Xun Wu:** Investigation, Data curation. **Ya-He Zhang:** Investigation. **Lin-Zhou Zhang:** Supervision, Project administration. **Quan Shi:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Sheng-Bao He:** Supervision. **Chun-Ming Xu:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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