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The Visbreaking of Heavy Oil in Supercritical Cyclohexane: The Effect of H-Donation

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Abstract: The performance of heavy oil visbreaking in supercritical cyclohexane ($_{SC}C_6H_{12}$) was evaluated, followed by a comparison with its reaction in supercritical benzene ($_{SC}C_6H_6$). The dealkylation-based viscosity reduction in the $_{SC}C_6H_{12}$ was accelerated by improving the diffusivity, through which a product viscosity (80 °C) as low as 0.5 Pa.s was readily obtained by visbreaking at 380 °C for 5 min. A competition between dealkylation and condensation took place throughout the visbreaking process. As the reaction proceeded or the temperature increased, condensation played an increasingly dominant role in the visbreaking. Unlike the inert $_{SC}C_6H_6$, the $_{SC}C_6H_{12}$ participated in the visbreaking by saturating the alkyl carbon radicals essential for dealkylation and the aromatic carbon radicals essential for condensation. The viscosity reduction efficiency of the visbreaking in the $_{SC}C_6H_{12}$ was initially suppressed by the H-donation of the solvent, but recovered rapidly due to the improved diffusion environment. Benefiting from the saturation of the aromatic carbon radicals, the asphaltene content of the product obtained in the $_{SC}C_6H_{12}$ was lower than the corresponding value of the product obtained in the $_{SC}C_6H_6$.

Keywords: visbreaking; heavy oil; supercritical cyclohexane; H-donation; dealkylation

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1. Introduction

According to the International Energy Agency, by 2030, oil demand will steadily increase from 11.6 million tons per day in 2010 to 14.5 million tons per day [1]. As the share of light crude oil in the remaining oil reserves declines, the utilization of unconventional heavy oil resources will become economically feasible. Heavy oils, including oil-sand bitumen, are dense materials with a viscosity of up to 10 Pa.s at ambient temperature. To meet the requirements for long-distance transportation, pretreatments involving viscosity reduction must be performed.

Visbreaking has been widely used in the petroleum processing industry. By maintaining a temperature of 400 to 500 °C in a coil or a soaker visbreaker for a certain residence time, the viscosity of visbreaking products is reduced [2,3]. However, the significant increase in asphaltene and olefin contents occurs simultaneously. Despite more than 100 years of application, the visbreaking technologies available are still characterized by low viscosity reduction efficiency and inferior product quality.

As with delayed coking, visbreaking also follows a free radical chain reaction mechanism [4]. The elementary reactions involved can be categorized into two reaction trends, namely dealkylation and condensation [5]. The former is responsible for the decomposition of heavy fractions and the viscosity reduction of visbreaking products, while the latter leads to the sequential condensation of oil fractions to coke. Based on the reported reaction kinetics data, Liu et al. found that dealkylation and condensation have a tandem structure at low temperatures and a parallel structure at high temperatures [6]. If dealkylation-based visbreaking is performed in a tandem structure, it is theoretically possible to suppress secondary condensation by terminating the visbreaking at an appropriate reaction time.

Unfortunately, due to the diffusion limitation on the reaction kinetics in the viscous oil phase, the efficiency of free radical reactions at low temperatures is extremely poor [7].

To alleviate the diffusion limitation caused by high viscosity to reaction kinetics, supercritical fluids (SCFs) showing gas-like transport properties (diffusivity and viscosity) and liquid-like density were applied to heavy oil visbreaking. Under ambient conditions, water is a typical polar solvent with a dielectric constant of 78. Due to the partial destruction of hydrogen bonds between water molecules, supercritical water ($_{SC}H_2O$, Tc = 374 °C, Pc = 22.1 MPa) becomes a non-polar solvent with a dielectric constant around 2 [8]. It has been confirmed that at a water-to-oil ratio higher than 3 and a water density higher than 0.25 g/mL, the visbreaking of heavy oil in the solvent of $_{SC}H_2O$ can be transferred into $_{SC}H_2O$ with dynamic viscosity as low as 10^{-5} Pa.s [6]. Since the diffusion coefficient of a substance is inversely proportional to the viscosity of the system, the diffusion coefficient of oil molecules in $_{SC}H_2O$ is about one to two orders of magnitude higher than that in the heavy oil. After alleviating the limitation of diffusion to reaction kinetics, an acceleration in viscosity reduction was observed at moderate temperatures of 390 to 420 °C. To verify the advantage of the tandem structure in visbreaking, supercritical benzene ($_{SC}C_6H_6$, Tc = 289 °C, Pc = 4.9 MPa) was also tried [9]. Benzene remaining thermally stable up to 550 °C is completely miscible with heavy oil under ambient conditions, so the mixture of heavy oil and $_{SC}C_6H_6$ should exist in the single-phase structure. Even at the temperature as low as 340 °C, the visbreaking in $_{SC}C_6H_6$ could be accomplished efficiently. At the same time, the formation of asphaltenes and olefins is suppressed. The combination of the tandem structure with SCFs with improved diffusivity offers a good opportunity to overcome the drawbacks of traditional visbreaking technologies.

To increase the feasibility of SCF visbreaking technologies, environmentally friendly solvents and mild operating conditions are required. $_{SC}H_2O$ is too harsh for industrial operations, while $_{SC}C_6H_6$ is highly toxic. It should be noted that some light alkanes are produced during visbreaking. If supercritical light alkanes are used as the solvents for visbreaking, the reaction can proceed without external solvent intervention. Even if $_{SC}H_2O$ or $_{SC}C_6H_6$ is still used as the solvent, the recycling of the solvent must be considered during continuous industrial operations. Therefore, light alkanes are inevitably mixed into the solvent. Unlike inert benzene and water, light alkanes may participate in visbreaking. Based on these considerations, the understanding of visbreaking in the presence of supercritical alkanes is critical for the industrial application of supercritical visbreaking technology. However, this important issue has not been studied in academia.

Herein, the reaction behavior of heavy oil visbreaking in supercritical cyclohexane ($_{SC}C_6H_{12}$, Tc = 280.4 °C, Pc = 4.1 MPa) was studied. The viscosity reduction performance under various $_{SC}C_6H_{12}$ environments was measured first, followed by the characterization of the properties of the obtained products. By comparing this with the visbreaking in $_{SC}C_6H_6$, the effect of H-donation on the unique visbreaking behavior in the $_{SC}C_6H_{12}$ solvent is further discussed. Through this study, it is hoped that the effects of supercritical solvents with different physical and chemical properties on heavy oil visbreaking can be further understood from the perspective of the phase structure, diffusion, and reaction mechanism.

2. Experimental Procedure

2.1. Apparatus and Reaction Runs

In order to compare the visbreaking in different SCFs, a heavy oil used in previous work was also used here [6,9]. For simplicity, the raw heavy oil provided by Sinopec Changling Refining and Chemical Company is referred to as Changling VR in the following text. Table 1 lists some basic properties of the raw heavy oil, and the symbols used in the table are explained in Nomenclature section. Changling VR has a high viscosity, which can only be measured at a temperature of 120 °C or higher.

Table 1. Properties of raw heavy oil.

H/C	**μ (Pa.s)** [a]	**Mn (Da)**	***CII***	**SARA Fractions (wt%)**			
1.54	**1.78**	**825**	**0.29**	**Saturates** **17.5**	**Aromatics** **52.4**	**Resins** **25.1**	**Asphaltenes** **5.0**
C residue (wt %)	C_S (%)	C_A (%)	olefin content (mol%)	R_A	R_N	L	N_{chains}
18.6	70.9	29.1	0	5.1	0.8	4.0	10.7

[a] Viscosity measured at 120 °C.

The visbreaking of Changling VR in the solvent of $_{SC}C_6H_{12}$ was applied in a Parr 4598-HPHT autoclave (Parr Instrument Company, USA), as shown in Figure 1. The autoclave, which had a capacity of 0.1 L, was made of SS 316 L steel and equipped with flat paddles. The temperature fluctuation during visbreaking could be controlled within ±3 °C.

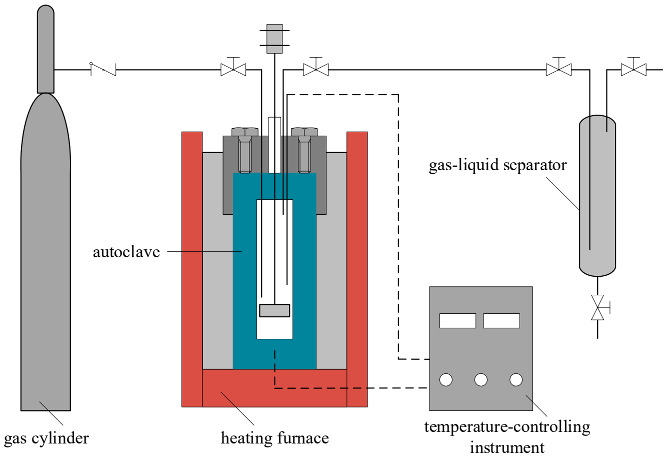

Figure 1. Schematic diagram of reaction device.

In a typical visbreaking operation under the $_{SC}C_6H_{12}$ environment, a certain amount of heavy oil and cyclohexane were first added into the autoclave. After purging with N_2 with a purity of 99.99%, the reactor was sealed and heated from room temperature to a preset temperature at a slope of 15 °C/min. The moment the temperature reached the preset value was determined to be the onset of visbreaking. To obtain a uniform temperature distribution in the reactor, the stirring rate was kept at 200 rpm during preheating and 800 rpm during visbreaking. Finally, the visbreaking for a given reaction time was quenched by immersing the reactor body in a water bath. Visbreaking was also performed under a specific $_{SC}C_6H_6$ environment, that is, a temperature of 380 °C, a solvent-to-heavy-oil ratio of 3:1 (wt) and a solvent density of 0.25 g/mL. The operating procedure was the same as that under the $_{SC}C_6H_{12}$ environment.

2.2. Analytical Procedures

After visbreaking in $_{SC}C_6H_{12}$, the autoclave was thoroughly washed with dichloromethane to collect products. If any solid coke was present, it was first removed by filtration. Dichloromethane and cyclohexane were then separated from the liquid product by vacuum rotary evaporation at temperatures of 30 and 50 °C, respectively. The separation of the visbreaking product obtained under the $_{SC}C_6H_6$ environment was similar to that under the $_{SC}C_6H_{12}$ environment.

Petroleum fractions and products can be characterized by their group composition or boiling-point distribution. Through elution with different solvents, the raw heavy oil and visbreaking products were separated into saturates, aromatics, resins, and asphaltenes (SARA fractions) in a column packed with Al_2O_3. The SARA separation follows the standard of Chinese Oil and Gas SY/T 5119 − 2016. Simulated distillation is a gas chromatography (GC) method in which oil samples are separated in a non-polar chromatographic column in order of their boiling points. In this work, the simulated distillation of the oil samples was applied on an Agilent 7890 GC (Agilent Technologies, Inc., Santa Clara, CA, USA) based on the standard of ASTM D2887.

Valid visbreaking operations were defined as experiments with a coke yield of less than 0.1 wt%. At this point, gas production was negligible. The mass balance of the visbreaking products consisting of liquid SARA fractions was usually higher than 98%. The yields of SARA fractions (Y_i) were evaluated by

$$Y_i = m_i / m_{raw} \times 100\% \tag{1}$$

where m_i denotes the weight of the collected SARA fractions and m_{raw} is the weight of the loaded raw heavy oil.

The colloidal instability index (CII) of raw heavy oil and visbreaking products was calculated by [10]:

$$CII = \frac{m_{saturates} + m_{asphaltenes}}{m_{aromatics} + m_{resins}} \tag{2}$$

Based on nuclear magnetic resonance (NMR) analyses, the olefin content (mol%) of raw heavy oil and visbreaking products was calculated by [11]

$$Olefin\ content = \sum \frac{A_i W_S M \times 4}{A_S W M_S N_i} \times 100\% \tag{3}$$

where A_S and A_i are the peak areas of the hydrogen atoms of dichloroethane added as internal standards and the specific type of hydrogen atoms contained in oil samples on the ^{1}H-NMR spectra. W_S and W are the weights of dichloroethane and oil samples. M_S and M are the molecular weights of dichloroethane and oil samples. N_i is the number of the specific types of hydrogen atom contained in oil samples.

The dynamic viscosity of oil samples was measured on an Advanced Rheology Expand System (TA Instruments). Except for the raw heavy oil, the dynamic viscosity of the visbreaking products was measured at a temperature of 80 °C. The GC-mass spectrometer (GC-MS) analysis of oil samples was performed on an Agilent 7890A-5975C. The elemental analysis of oil samples was applied on a Vario EL III element analyzer. The number average molecular weight of oil samples was characterized on a KNAUER K7000 vapor pressure osmometer (VPO, Knauer, Germany) based on the China Petrochemical standard SH/T 0583–94. The H-NMR and C-NMR spectra of oil samples were obtained on a Bruker AVANCE 400 MHz NMR Spectrometer (Bruker Corporation, Switzerland).

3. Results and discussion

3.1. Dealkylation-Based Viscosity Reduction under $_{SC}C_6H_{12}$ Environments

The viscosity reduction under various $_{SC}C_6H_{12}$ environments was evaluated through three series of experiments, in which one of the operating variables of temperature, $_{SC}C_6H_{12}$-to-heavy-oil ratio, and $_{SC}C_6H_{12}$ density changed and the other two variables were fixed. The results are shown in Figure 2.

At the applied temperature ranging from 360 to 390 °C, the product viscosity decreased along with the extension of reaction time. As the temperature increased, the viscosity of the visbreaking product obtained at the same reaction time decreased monotonically. An acceptable product viscosity around 0.50 Pa.s could be obtained after 5 min of reaction at a temperature of 380 °C, an $_{SC}C_6H_{12}$ density of 0.25 g/mL, and a $_{SC}C_6H_{12}$-to-heavyoil ratio of 3:1 (wt). By contrast, visbreaking under N_2 environments requires a temperature above 390 °C and a reaction time of more than 30 min to achieve similar viscosity reduction performance [6]. It is worth noting that the reaction time required for coke formation is reduced as the temperature increases. At a temperature of 390 °C, only at a reaction time of 0 min can a valid product be obtained. Obviously, an increase in reaction temperature accelerates both dealkylation and condensation. With a higher apparent reaction barrier, the latter dominates the visbreaking at high temperatures.

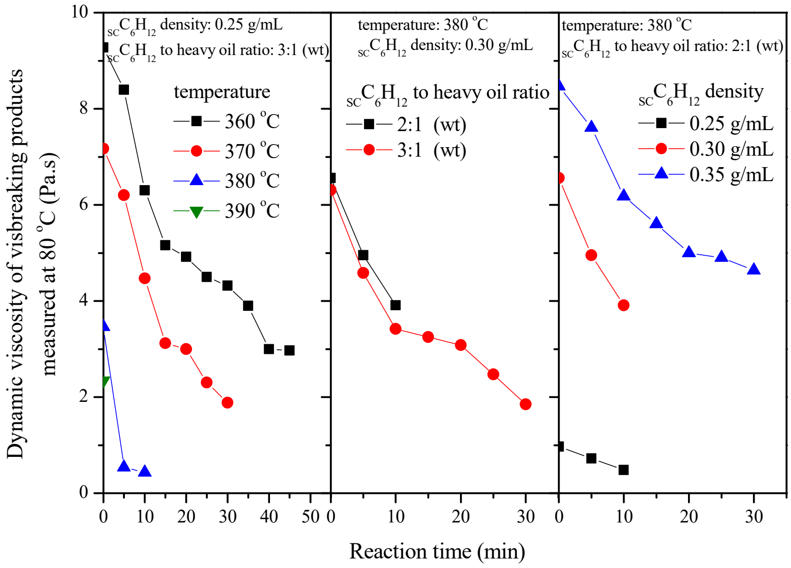

Figure 2. Viscosity reduction in heavy oil under various $_{SC}C_6H_{12}$ environments.

The visbreaking at varying $_{SC}C_6H_{12}$-to-heavy-oil ratios or $_{SC}C_6H_{12}$ densities partially reflected the effect of the diffusivity on the reaction kinetics. Increases in the $_{SC}C_6H_{12}$-to-heavy-oil ratio improved the diffusivity of the heavy oil molecules but reduced the heavy oil concentration in the reaction system. When the $_{SC}C_6H_{12}$-to-heavy-oil ratio increased from 2:1 to 3:1 (wt), the viscosity reduction was accelerated slightly. If the dealkylation rate was simply described by a power law model, the positive effect of the diffusion improvement on the apparent reaction-rate constant should have exceeded the adverse effect of the decreasing heavy oil concentration on the dealkylation kinetics. Due to the extended reaction time required to obtain valid visbreaking products, one may propose that condensation kinetics are more sensitive to the concentration of heavy oil than dealkylation kinetics.

According to the reported visbreaking in $_{SC}C_6H_6$ and $_{SC}H_2O$ at increasing solvent density, the unfavorable cage effect on dealkylation kinetics could be effectively compensated by improving diffusivity [6,9]. Similarly, it was expected that accelerated viscosity reduction would be observed with the increase in the $_{SC}C_6H_{12}$ density. However, the experimental results showed a trend that was contrary to expectations. By increasing the density of the $_{SC}C_6H_{12}$ from 0.25 to 0.35 g/mL, the viscosity reduction was significantly delayed. At the same time, the reaction time required to obtain valid visbreaking products was extended from 10 min at a solvent density of 0.25 g/mL to 30 min at a solvent density of 0.35 g/mL. That is to say, both the dealkylation and the condensation were suppressed at the increasing $_{SC}C_6H_{12}$ density.

3.2. Competition between Dealkylation and Condensation during Visbreaking

The presence of condensation limits the depth of viscosity reduction. To understand the relationship between dealkylation and condensation under a $_{SC}C_6H_{12}$ environment, that is, a temperature of 360 °C, a solvent density of 0.25 g/mL, and a solvent-to-heavy-oil ratio of 3:1 (wt), the visbreaking products obtained at the extended reaction time were characterized by simulated distillation GC, SARA distribution, and molecular weight analyses. The results are presented in Figure 3a and Table 2.

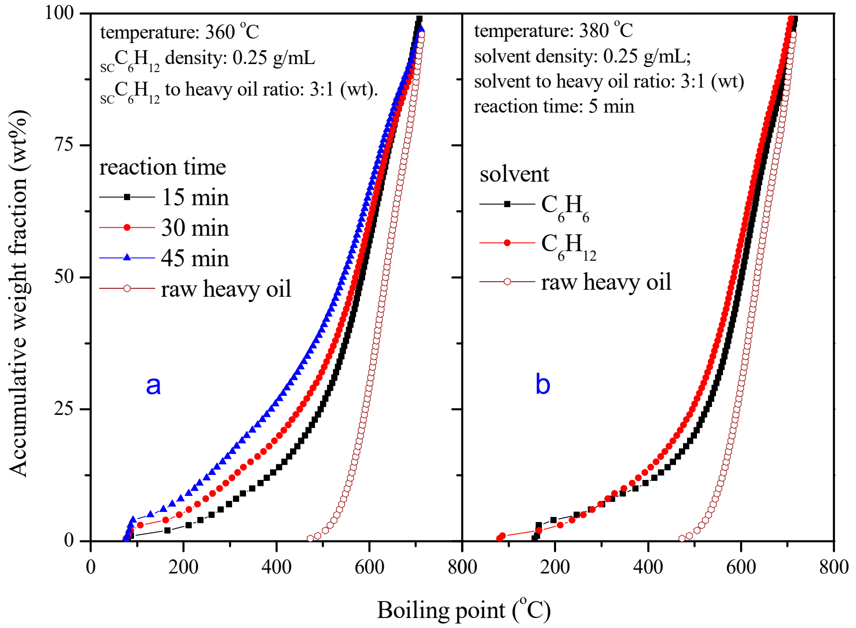

Figure 3. Boiling-point distribution of visbreaking products. (**a**) Visbreaking in $_{SC}C_6H_{12}$ at extended reaction time and (**b**) visbreaking in different SCF solvents.

Table 2. Properties of visbreaking products obtained in $_{SC}C_6H_{12}$. Temperature of 360 °C, $_{SC}C_6H_{12}$-to-heavy-oil ratio of 3:1 (wt), and $_{SC}C_6H_{12}$ density of 0.25 g/mL.

Reaction Time (min)	**Mn**	**SARA Fraction (wt%)**				***CII***	**Olefin Content (mol%)**
		Saturates	**Aromatics**	**Resins**	**Asphaltenes**		
-	825	17.5	52.4	25.1	5.0	0.29	0
15	662	15.4	54.7	20.3	9.6	0.33	14.2
30	602	17.3	49.4	19.7	13.6	0.45	18.1
45	696	13.1	46.9	26.2	13.8	0.37	25.4

After the visbreaking in the $_{SC}C_6H_{12}$, the initial boiling point (IBP) of the visbreaking products decreased sharply from 474 to about 76 °C. Because of the continuous dealkylation-based decomposition of the heavy fractions, the percentage of non-VR fractions with boiling points lower than 500 °C in the products increased steadily along with the extension of the reaction time.

However, the SARA distribution suggests the occurrence of condensation throughout the visbreaking process. Regardless of the decomposition of the resins and the decrease in the average molecular weight of the visbreaking products in the early reaction stage, the fraction of asphaltenes nearly doubled at the reaction time of 15 min. As the reaction proceeded, condensation played an increasingly important role in the visbreaking. At the reaction time of 45 min, the average molecular weight of the liquid product no longer decreased but instead increased. The simultaneous decrease in the fractions of the saturates and aromatics at that time shows that even light fractions participate in condensation in the middle and late visbreaking stages. Eventually, the fraction of asphaltenes in the visbreaking product can be as high as 13.8 wt%.

Because of the evolution of the SARA distribution, the CII value of the visbreaking product increased up to 0.45, indicating the decreasing stability of the colloidal structure of the asphaltenes. In the meantime, the olefin content increased from 0 to 25.4 mol%. From a reaction-engineering point of view, even if visbreaking is performed in the advantageous tandem structure, an extension of the reaction time definitely leads to the occurrence of secondary condensation and the excessive β-scission of alkyl substitutes of aromatics.

To suppress asphaltene and olefin production, it is necessary to selectively accelerate dealkylation and shorten the reaction time for dealkylation.

3.3. Difference in Visbreaking Behavior in Various SCFs

The purpose of introducing SCFs in heavy oil visbreaking is to transfer the reaction to SCFs with excellent diffusivity. Combined with literature reports, the effectiveness of process enhancement in various SCFs can be demonstrated [6,9]. Unlike benzene and cyclohexane, water shows good mutual solubility with heavy oil only in the supercritical region. Unfortunately, the critical conditions of water are far harsher than those of benzene and cyclohexane. Therefore, visbreaking in $_{SC}H_2O$ must be performed at pressures above 22 MPa, while the visbreaking pressure in $_{SC}H_6H_6$ or $_{SC}H_6H_{12}$ varies between 8 and 10 MPa. To ensure the mutual solubility of $_{SC}H_2O$ and heavy oil, the temperature used for visbreaking in $_{SC}H_2O$ is 20 to 30 °C higher than the reaction temperature in other SCF solvents. Nevertheless, the reported optimum temperature of 400 °C is well below that required for H_2 production from heavy oil reforming in hydrothermal environment. Reforming typically operates at temperatures above 1000 °C [12].

Since benzene and cyclohexane are very similar in terms of their physical properties, the visbreaking in the $_{SC}C_6H_6$ and $_{SC}C_6H_{12}$ was further compared in order to distinguish the specificity of the visbreaking behavior in the $_{SC}C_6H_{12}$. Table 3 lists the dynamic viscosity and SARA distribution of the visbreaking products obtained at the temperature of 380 °C, solvent-to-heavy-oil ratio of 3:1 (wt), and solvent density of 0.25 g/mL.

Table 3. Dynamic viscosity and SARA distribution of visbreaking products obtained in $_{SC}C_6H_6$ and $_{SC}C_6H_{12}$. Temperature of 380 °C, solvent-to-heavy-oil ratio of 3:1 (wt), and solvent density of 0.25 g/mL.

Solvent	**Reaction Time (min)**	***μ* (Pa.s), 80 °C**	**SARA Fractions (wt%)**			
			Saturates	**Aromatics**	**Resins**	**Asphaltenes**
-	-	-	17.5	52.4	25.1	5
$_{SC}C_6H_{12}$	0	3.46	17.3	51.9	22.7	8.1
	5	0.54	14.5	49.4	26.0	10.1
	10	0.43	12.3	49.3	28.0	10.4
$_{SC}C_6H_6$	0	1.16	17.5	53.4	19.1	10.0
	5	0.52	14.2	47.9	24.2	13.7
	10	0.41	5.7	55.6	23.9	14.8

The efficiency of the viscosity reduction varied greatly under different solvent environments. In the solvent of the $_{SC}C_6H_6$, the product viscosity rapidly decreased to 1.16 Pa.s at the reaction time of 0 min. As the reaction time was extended to 10 min, the product viscosity was further reduced to 0.40 Pa.s. The initial viscosity reduction efficiency in the $_{SC}C_6H_{12}$ was significantly lower than that in the $_{SC}C_6H_6$, but the same product viscosity was achieved at the reaction time of 5 or 10 min. Due to the occurrence of condensation, the fraction of the asphaltenes in either the $_{SC}C_6H_6$ or the $_{SC}C_6H_{12}$ increased steadily with the extension of the reaction time. The condensation to asphaltenes in the $_{SC}C_6H_{12}$ was slower than in the $_{SC}C_6H_6$, suggesting that the presence of $_{SC}C_6H_{12}$ solvent can partially suppress both dealkylation and condensation.

The results of the simulated-distillation GC analysis shown in Figure 3b indicate that there was a subtle difference between the products obtained in the $_{SC}C_6H_{12}$ and the $_{SC}C_6H_6$. At first glance, satisfactory upgrading can be achieved by visbreaking in any applied solvent. The percentage of non-VR fractions in the visbreaking products obtained in $_{SC}C_6H_{12}$ and $_{SC}C_6H_6$ increased by 23 and 28 wt%, respectively. However, the IBP of the product obtained in the $_{SC}C_6H_{12}$ was about 80 °C lower than that obtained in the $_{SC}C_6H_6$. According to the GC-MS analysis, a small number of C_6-C_9 fractions, mainly cyclohexene, *n*-heptane, methyl cyclohexane, 2-methyl heptane, 2,3-dimethyl heptane, and 1,1-dimethyl-

3-methyl cyclohexane, were detected in the product obtained in the $_{SC}C_6H_{12}$. These light fractions, which had a boiling point of less than 150 °C, accounted for about 1.0 wt% of the visbreaking product. In the blank experiments on the stability of cyclohexane, only the isomerization products of cyclohexane, such as 2-methylpentane, 3-methylpentane, *n*-hexane, and methyl-cyclopentane could be detected after 30 min of thermal treatment at temperatures of 360 to 390 °C.

Combined with the reports on visbreaking in $_{SC}H_2O$, it was confirmed that the principle of SCF intervention in heavy oil visbreaking is similar [6]. With the tandem structure of dealkylation and condensation, the precedent dealkylation that determines viscosity reduction and light oil production can be accelerated by transferring the reaction from viscous heavy oil into SCFs with superior diffusivity. Furthermore, the undesired secondary condensation can be suppressed through the timely termination of visbreaking at an optimized reaction time. Nevertheless, in terms of the suppressed dealkylation at increasing $_{SC}C_6H_{12}$ density, the restricted asphaltene formation, and the production of low-boiling-point light fractions, one may suggest that $_{SC}C_6H_{12}$ is involved in heavy oil visbreaking through a specific mechanism.

3.4. Effect of H-Donation of $_{SC}C_6H_{12}$ on Visbreaking

Benzene is essentially an inert reaction medium for heavy oil visbreaking because only methyl radicals are capable of abstracting H atoms from aromatic rings [13]. By contrast, the H-abstraction between cyclohexane and alkyl carbon radicals may occur with a moderate reaction barrier of 30 to 87 kJ/mol [14–16]. Furthermore, it was reported that the pyrolysis of heavy oil could be retarded by the presence of the solvent capable of donating H_β atoms [17–19]. Based on the generally accepted free radical chain reaction mechanism of thermal processing, the effect of the H-donation of $_{SC}C_6H_{12}$ on the propagation of the dealkylation network is schematically shown in Figure 4 [4,20].

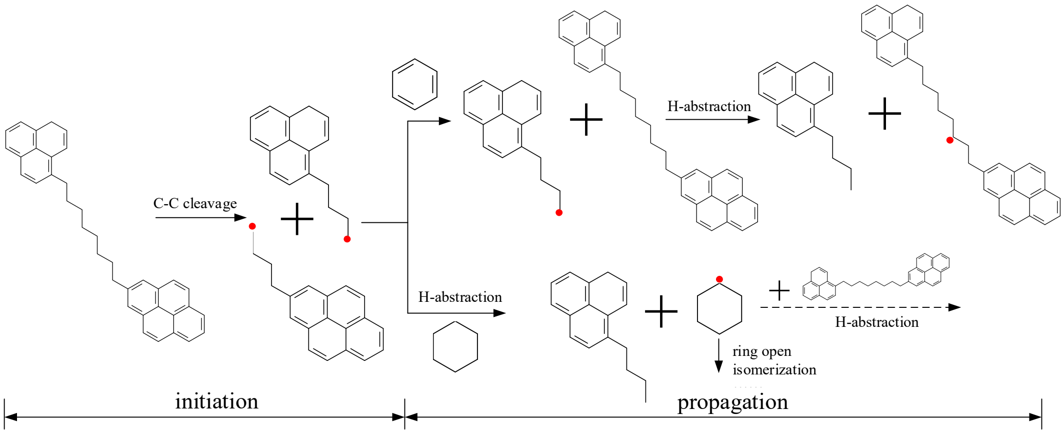

Figure 4. Schematic diagram of initiation and propagation of dealkylation network in $_{SC}C_6H_6$ or $_{SC}C_6H_{12}$.

During the visbreaking of heavy oil, the alkyl substitutes of aromatics decompose first at temperatures higher than 325 °C, at which point primary alkyl carbon radicals are formed. Depending on the location of the C-C cleavage, the corresponding reaction barrier could vary around 317 kJ/mol [21]. The following propagation of the dealkylation network was accomplished by the reactions as follows: H-abstraction between the primary alkyl carbon radicals and the alkyl substitutes of other heavy oil molecules, and the β-scission of the formed secondary alkyl carbon radicals [9]. The propagation of dealkylation involves a large number of bimolecular reactions; therefore, the apparent reaction kinetics of dealkylation are sensitive to the diffusivity of the surroundings [22]. Benefiting from the excellent diffusivity in SCFs, the propagation of dealkylation is accelerated and the viscosity reduction efficiency is improved accordingly.

With the introduction of $_{SC}C_6H_{12}$, the primary alkyl carbon radicals essential for the propagation of the dealkylation network are likely to be saturated by abstracting the H atoms in cyclohexane. To examine whether the formed naphthenic carbon radicals can continue the propagation of dealkylation, their activity was evaluated in terms of the Fukui index. The higher the Fukui index, the more active the radicals [23]. Using a calculation based on the open-shell B3LYP density functional, the Fukui indices of the naphthenic carbon radicals and primary alkyl carbon radicals, shown in Figure 4, were found to be 0.326 and 0.381, respectively. Therefore, the propagation efficiency of dealkylation was reduced by the saturation of the primary alkyl carbon radicals and the formation of the less active naphthenic carbon radicals.

Although the viscosity reduction was delayed by the H-donation of the $_{SC}C_6H_{12}$, the aromatic carbon radicals that are essential for condensation were saturated in the same way [13,24]. Through a comparison of the average molecular structure parameters of the visbreaking products obtained in the $_{SC}C_6H_{12}$ and $_{SC}C_6H_6$, the dealkylation responsible for the viscosity reduction in any of the SCFs and the suppressed condensation in the $_{SC}C_6H_{12}$ was further verified. The visbreaking products shown in Table 2 were characterized using elemental analysis, VPO measurement, and NMR characterization. The average molecular structure of the visbreaking products was then calculated according to the modified Brown−Ladner formula, with the results listed in Table 4 [25–27].

Table 4. Average molecular structure parameters of liquid visbreaking products obtained in $_{SC}C_6H_6$ or $_{SC}C_6H_{12}$. Temperature of 380 °C, solvent-to-heavy-oil ratio of 3:1 (wt), and solvent density of 0.25 g/mL.

Solvent	Reaction Time (min)	C_S (%)	C_A (%)	R_A	R_N	$N_{chains} \times L$
-	-	70.9	29.1	5.1	0.8	42.8
$_{SC}C_6H_{12}$	0	67.6	32.4	7.3	0.8	42.0
	5	65.6	34.4	7.1	0.7	33.6
	10	63.0	37.0	6.5	0.7	28.5
$_{SC}C_6H_6$	0	66.8	33.2	6.3	0.8	35.0
	5	64.6	35.4	6.1	0.7	29.3
	10	62.1	37.9	5.8	0.7	24.6

The average molecular structure of the visbreaking products obtained in the $_{SC}C_6H_{12}$ and $_{SC}C_6H_6$ evolved with a similar trend. The naphthenic structure, reflected by the average number of naphthenic rings contained in the heavy oil molecules (R_N), varied slightly throughout the visbreaking process. By contrast, the occurrence of dealkylation, indicated by the substantial variation in the product of the average number of alkyl substitutes (N_{chains}) and the average length of the alkyl substitutes (L), was clearly observed. Through dealkylation, the average number of aromatic rings (R_A) in the visbreaking product decreased in the early visbreaking stage. On the basis of the continuously increasing fraction of aromatic carbon atoms in the product (C_A), condensation was inevitable, even when the favorable tandem structure of dealkylation and condensation was applied. The value of C_A of the visbreaking product obtained in the $_{SC}C_6H_{12}$ was systematically lower than that obtained in the $_{SC}C_6H_6$, confirming the partially suppressed condensation in the $_{SC}C_6H_{12}$.

4. Conclusions

By removing the limitation of diffusion on the reaction kinetics, the visbreaking of heavy oil in $_{SC}C_6H_{12}$ can be accomplished efficiently at a moderate temperature, of around 380 °C. The visbreaking performance is sensitive to the variation in the reaction temperature, solvent-to-heavy-oil ratio, and solvent density. Even with a favorable tandem structure, secondary condensation plays an increasingly dominant role in visbreaking as the temperature increases or the reaction proceeds. Regardless of which supercritical fluid is introduced, all fluids provide excellent diffusion environments for heavy oil visbreaking.

Compared with $_{SC}C_6H_6$ and $_{SC}H_2O$, the special characteristic of $_{SC}C_6H_{12}$ is that the solvent is involved in the reaction through H-donation. As a H-donor, $_{SC}C_6H_{12}$ participates in visbreaking by saturating the carbon radicals that are essential for dealkylation and condensation. Compared with the visbreaking in inert $_{SC}C_6H_6$, the visbreaking in $_{SC}C_6H_{12}$ is characterized by a delayed initial viscosity reduction efficiency and reduced asphaltene formation. Light alkanes are parts of heavy oil visbreaking products, and cyclohexane is one of the representative components of light alkanes. The application of supercritical alkanes as solvents for heavy oil visbreaking has significant advantages over $_{SC}H_2O$ and $_{SC}C_6H_6$ in terms of environmental friendliness, milder operating conditions, and improved product distribution.

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Abbreviations

C_A	fraction of aromatic carbon atoms in total carbon atoms contained in oil samples, %
C_S	fraction of non-aromatic carbon atoms in total carbon atoms contained in oil samples, %
CII	colloidal instability index of asphaltenes in oil samples
m_i	weight of collected SARA fractions in visbreaking product, g
m_{raw}	weight of loaded raw heavy oil, g
M_n	number average molecular weight of oil samples, Da
L	average length per alkyl substituent
Y_i	weigh fraction of SARA fractions collected
R_A	average number of aromatic rings per average oil molecule
R_N	average number of naphthenic rings per average oil molecule
N_{chains}	average number of alkyl substituents per average oil molecule
μ	dynamic viscosity of oil samples, Pa.s

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