

Mechanisms of CO₂ and water soluble sodium-based catalysts in the aquathermolysis of heavy oil

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ABSTRACT

The application of carbon dioxide (CO₂) for heavy oil extraction presents a promising alternative, particularly in scenarios where conventional techniques prove economically unviable. This study analyzes the effects of non-catalytic thermolysis at various initial CO₂ pressures, both with and without water (H₂O), aiming to identify optimal conditions for reducing the viscosity of heavy oil. These conditions are subsequently applied within the framework of catalytic aquathermolysis with a water-soluble catalyst at a temperature of 300 °C for 24 h. The obtained results demonstrate that increasing the initial CO₂ pressure leads to improved solubility and swelling of conversion products, which, in turn, contributes to the reduction of viscosity. During catalytic thermolysis with water-soluble catalysts based on Na₃VO₄, NaH₂PO₄, and Na₂H₅P(W₂O₇)₆ in a CO₂ atmosphere, a high level of efficiency was recorded for the Na₃VO₄ catalyst under optimal conditions, resulting in a 35.5 % reduction in asphaltene content, as well as a 72.8 % reduction in viscosity at 20 °C and a 41.2 % decrease in sulfur content compared to heavy oil. Moreover, the inclusion of tetralin in the process as a hydrogen donor significantly enhanced the reduction of viscosity and increased the yield of light fractions such as gasoline and diesel fuel. The results of the work emphasize the high promise of combining CO₂ with water-soluble catalysts in catalytic aquathermolysis for reducing the viscosity of heavy oil. This opens new opportunities for improving processing efficiency and could significantly impact the future of the oil industry.

1. Introduction

In recent years, the oil industry has faced the depletion of easily accessible reserves, necessitating the production of heavy oil, which, although more available, presents a number of challenges. Heavy oil is characterized by its high density and high content of asphaltenes and heteroatoms, complicating its extraction and processing, and consequently increasing costs [1]. Effective development of heavy oil resources is critical to meeting future energy needs [2]. To enhance the efficiency of heavy oil extraction, focus is placed on thermal methods such as steam injection, cyclic steam stimulation (CSS), and steam-assisted gravity drainage (SAGD) [3]. These technologies aim to raise reservoir temperatures, thereby reducing oil viscosity and improving flow, facilitating more efficient extraction. In the early stages of heavy oil development, thermal production is notably beneficial. However, issues arise due to the heterogeneity of heavy oil reservoirs and the characteristics of wet saturated steam, such as significant heat loss of

steam at later development stages and a gradual decline in the effectiveness of multiple development cycles, which significantly reduces economic efficiency [4].

To ensure the sustainability of the heavy oil industry, the development of effective technologies that replace traditional methods is necessary. Recently, there has been an increasing interest in the use of non-hydrocarbon gases in thermal extraction methods. Carbon dioxide (CO₂) demonstrates high solubility in heavy oil, which leads to an effective reduction in its viscosity and, consequently, improves its mobility in the reservoir [5]. The use of CO₂ in combination with steam injection during heavy oil production not only compensates for reservoir energy and increases extraction efficiency without reducing temperature but also facilitates the utilization of CO₂, thereby reducing costs for steam injection. Field tests conducted by Cheng et al. showed that using CO₂ instead of water during injection can increase oil recovery by 10 % [6]. The study by Sohrabi et al. showed that the use of CO₂ is more effective than water-bearing methods, increasing oil recovery by 30 %

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with the alternative injection of CO₂ and steam [7]. The primary mechanism by which carbon dioxide affects heavy oil is through the formation of an “oil-in-gas” type emulsion resulting from CO₂ injection. This results in a significant reduction in the viscosity of heavy oil and an increase in its permeability within porous media [8]. Chanmoly Or et al. conducted experiments demonstrating that reducing the pressure of heavy oil saturated with carbon dioxide (from 9.97 MPa to below 8.0 MPa at a temperature of 50 °C) resulted in the formation of foamy oil. This oil exhibited a significant volume increase (from 36.8 % to 47.5 %) and a notable decrease in viscosity from 79 % to 42 % of the original value [9].

Water-soluble catalysts are actively researched in the field of heavy oil processing, including aquathermolysis and hydrotreatment processes, which significantly enhance the quality of final products and increase the efficiency of hydrocarbon processing. Yantao Zhou et al. studied the application of the NaOH/CuSO₄ catalyst to improve the quality of heavy oil through aquathermolysis. CuSO₄ increased viscosity, but the addition of NaOH reduced it by 81.43 % at 300 °C, inhibiting reactions caused by CuSO₄ and enhancing the integration of copper into oil molecules [10]. Yasser I. I. et al. investigated the catalytic efficiency of water-soluble catalysts NiSO₄ and FeSO₄, which led to a reduction in viscosity by 50 % and 60 %, respectively, compared to the viscosity of heavy oil. Tetralin is an effective hydrogen donor because its structure contains four saturated hydrocarbon rings [11]. At high temperatures and pressures, tetralin is capable of releasing hydrogen, transforming into the more stable naphthalene. This process is accompanied by the breaking of C-H bonds in tetralin and the subsequent transfer of the generated hydrogen to reactive fragments of heavy oil molecules [12,13].

The combination of carbon dioxide (CO₂) with water-soluble catalysts is a promising approach to upgrading heavy oil, enhancing the efficiency and selectivity of refining processes while reducing the negative impact on the environment, thus making these processes safer and more environmentally friendly.

This study focuses on addressing the gap in the current scientific literature regarding heavy oil processing. Unlike existing works that primarily focus on the application of CO₂ or water-soluble catalysts separately, this article presents the results of studying their combined effect on the process of aquathermolysis, as well as demonstrating the mechanism and results of this process. For the first time, the study examines the influence of water-soluble catalysts, such as NaH₂PO₄, Na₃VO₄, and Na₂H₅P(W₂O₇)₆, in combination with carbon dioxide to enhance the efficiency of heavy oil processing. The literature lacks studies dedicated to exploring this combined methodology, making the presented work innovative. Furthermore, the novelty lies in conducting a comparative analysis of the thermal cracking process with a unique combination of CO₂ and a specific volume of water, as well as with catalytic thermolysis. The detailing of the mechanism and specific experimental conditions presented in this work has not been covered in the scientific literature before. Such conditions and their impact on the heavy oil processing are unique and represent a significant contribution to the development of scientific knowledge in this field.

The aim of this study is to determine the optimal conditions for the aquathermolysis of heavy oil using carbon dioxide at various pressures in the presence and absence of water, as well as to evaluate the effectiveness of water-soluble sodium-based catalysts for improving the upgrading process of heavy oil.

To achieve this goal, oil samples were processed in a high-pressure autoclave at a temperature of 300 °C for 24 h. The obtained products were analyzed using a variety of analytical methods, enabling a comparison with the characteristics of the initial raw oil sample.

The results of this study will provide a scientific basis for the application of NaH₂PO₄ and Na₃VO₄ in a CO₂ environment for the hydrothermal treatment of heavy oil, opening up prospects for their widespread use in the near future. Furthermore, the obtained data may significantly improve existing enhanced oil recovery (EOR) strategies,

which is crucial for optimizing hydrocarbon extraction processes.

2. Experimental

2.1. Materials

The heavy oil samples used in this study were sourced from the Ashal'cha field located in the Republic of Tatarstan, Russia. The characteristics of heavy oil are outlined in Table 1.

2.2. Experiment conditions

Laboratory modeling of the aquathermolysis process was carried out using a 300-ml high-pressure reactor (Fig. 1). The reaction mixture consisted of: heavy oil + CO₂ ± H₂O ± catalyst ± tetralin in the mass ratio indicated in Table 2. Then the reactor was sealed and purged with CO₂ for 10 min to remove air. Next, CO₂ was introduced into the autoclave to create an initial pressure in the range of 10–40 bar. The reactor was then heated to 300 °C for approximately 35 min and maintained at this temperature for 24 h, resulting in a final pressure of approximately 20–110 bar. Subsequently, the mixture of products was cooled to 25 °C to stop the reaction. After the process was completed, the oil was initially separated from the water by settling for 48 h, followed by centrifugation on the Eppendorf 5804R laboratory centrifuge at 3000 rpm for 2 h. After centrifugation, the anhydrous products were subjected to further analysis using various analytical methods. The oil sludge, along with the catalyst, was washed with toluene and separated on filter paper, which allowed for the complete purification of the samples for further study.

Table 2 shows the conditions of the experiments performed in the autoclave.

Laboratory studies on the upgrading of heavy oil (Table 2) were conducted in two stages: non-catalytic and catalytic thermolysis using water-soluble catalysts. The experiments were carried out as follows:

1. The first stage

– The study began with conducting experiments Ex(C10), Ex(C20), Ex(C30), and Ex(C40). These were carried out as independent investigations to assess the impact of different initial CO₂ pressures on the characteristics of heavy oil. In each experiment, a fresh sample of heavy oil weighing 50 g was loaded into the reactor. Before heating to 300 °C, the target initial CO₂ pressure was set according to each experiment (10, 20, 30, or 40 bar). After 24 h of exposure to high temperatures, a detailed analysis of the obtained data was conducted for each experiment, allowing for the identification of patterns and relationships associated with changes in the properties of heavy oil under various conditions.

– After that, the CO₂ pressure was reduced to 10 bar, and 20 g and 30 g of water were added to the reaction system. In the final stage, the pressure was again increased to 40 bar with the addition of 10 g of water (Blank(C40-H10)).

– The best results for reducing viscosity and changing the elemental composition of the oil were obtained at a CO₂ pressure of 40 bar (Ex(C40)) and at 40 bar CO₂ with the addition of 10 g of water (Blank(C40-H10)).

2. The second stage: The influence of water-soluble catalysts was studied under the optimal conditions identified in the first stage (Blank(C40-H10))

Fig. 2 shows the relationship between pressure and temperature in experimental systems when heated to 300 °C. In the sample Ex(C10) in CO₂ systems, there is an increase in pressure up to 20 bar with rising temperature due to the increase in the kinetic energy of the molecules and the strengthening of molecular interactions. Systems with CO₂ and water demonstrate higher pressure values due to the phase transition of water from liquid to gaseous state (evaporation) [14]. When comparing the samples Ex(C40-H10)NPW and Ex(C40-H10)NVT, an increase in pressure to 105 and 110 bar, respectively, is noted, indicating the

Table 1
Properties of the used heavy oil.

Parameter	Viscosity mPa·s, 20 °C	Elemental content (%)					SARA fractions (%)			
		C	H	N	S	O	saturates	aromatics	resins	asphaltenes
Error (±wt.%)	1	0.5	0.5	0.03	0.2	0.05	0.3	0.5	0.4	0.2
	4000	81.98	11.12	0.38	5.54	0.98	25.6	32.3	34.5	7.6

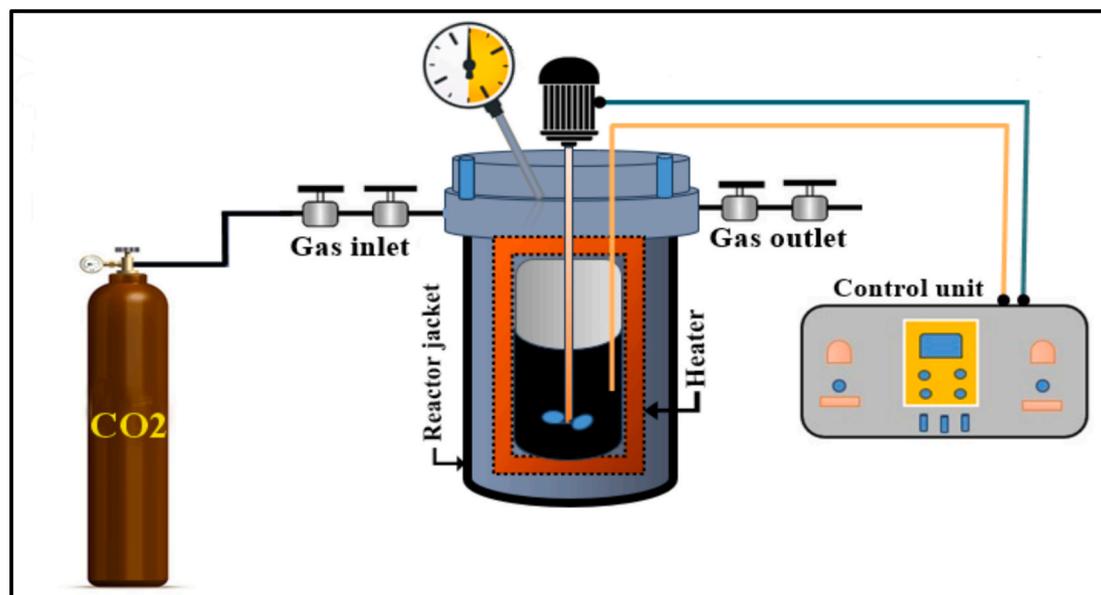


Fig. 1. Schematic representation of batch reactor for catalytic upgrading.

Table 2
Experimental Conditions. Heavy oil (50 g) + CO₂ ± H₂O ± catalyst (1 g) ± tetralin (1 g).

Samples	CO ₂ (bar)	H ₂ O (g)	Catalyst Content
Ex(C10)	10	–	–
Ex(C20)	20	–	–
Ex(C30)	30	–	–
EX(C40)	40	–	–
Ex(C10-H20)	10	20	–
Ex(C10-H30)	10	30	–
Blank(C40-H10)	40	10	–
Ex(C40-H10)NPW	40	10	Na ₃ H ₅ P(W ₂ O ₇) ₆
Ex(C40-H10)NP	40	10	Na ₃ H ₂ PO ₄
Ex(C40-H10)NV	40	10	Na ₃ VO ₄
Ex(C40-H10)NVT	40	10	Na ₃ VO ₄ + Tetralin

influence of catalytic systems on the dynamics of the processes. The differences in the observed pressure values suggest a significant impact of the nature of the catalyst on the rate and equilibrium of the reactions occurring in the system. Experiments conducted over 24 h show a continuous increase in pressure, highlighting the importance of the time factor in achieving thermodynamic equilibrium in CO₂ systems [15].

2.3. Analytical procedures

2.3.1. Viscosity measurements

Viscosity measurements (20–80 °C, 10 °C increments) of the initial and hydrothermally treated oils (with and without chemical agents) were performed using a FUNGILAB Alpha L rotational viscometer (TL5 spindle, 6.7 mL sample) equipped with a HUBER MPC K6 thermostat. Shear rate was calculated as 1.32*RPM (manual). RPM was adjusted for temperature and torque (50–90 %). The viscometer exhibited a relative error of ± 1.0 % and high reproducibility (<0.2 % deviation).

2.3.2. Sara-analysis

Heavy oil composition was determined using SARA analysis (GOST 32269–2013 and ASTM D 4124–09). Asphaltenes were precipitated from 1.0 g of oil using 40 volumes of n-hexane. Maltenes were separated into saturated hydrocarbons, aromatic hydrocarbons, and resins using a chromatographic column packed with neutral alumina (calcined at 450 °C for 3 h).

2.3.3. Ultimate analysis

The elemental composition of the heavy oils, both before and after upgrading, was analyzed using the Perkin Elmer 2400 Series II analyzer (Perkin Elmer, MA, USA). This instrument enables the measurement of carbon, hydrogen, nitrogen, oxygen, and sulfur content in the oil.

2.3.4. FTIR spectroscopy

To analyze the structural composition of oil, including resins and asphaltenes extracted before and after treatment, Fourier FT-IR spectroscopy was performed using a Bruker Tensor II FTIR instrument, achieving a resolution of 4 cm⁻¹ over a wavelength range of 400–4000 cm⁻¹.

2.3.5. Proton nuclear magnetic resonance

¹H NMR spectra were acquired using a Bruker Avance 400 spectrometer (400.1 MHz, CDCl₃ solvent) and FTIR spectra using a Bruker Tensor spectrometer (KBr plates).

2.3.6. Gas Chromatography-Mass Spectrometry (GC-MS)

The saturated and aromatic hydrocarbon fractions in heavy oil samples (both before and after aquathermolysis) were examined using GC/MS (Chromatek-Crystal 5000.2) equipped with a mass spectrometric detector (214.2.840.083–10 with an ADVIS ion source). Data processing was performed on total ion current as well as ions with *m/z* 57, which correspond to normal and *iso*-alkanes. For the analysis of

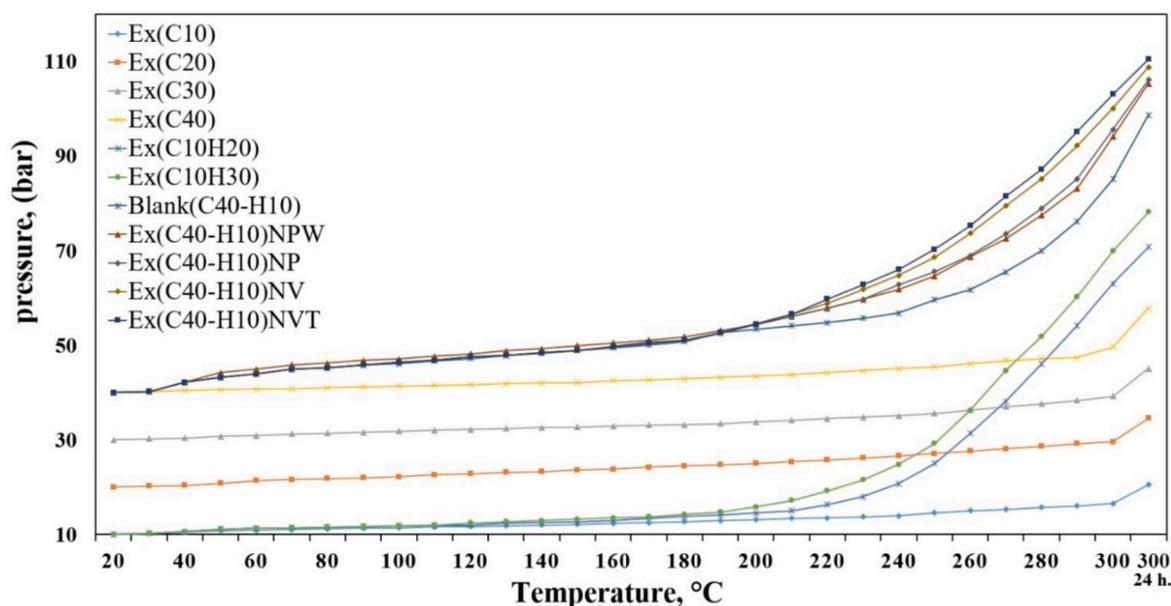


Fig. 2. Curved dependencies of pressure on temperature during thermocracking and catalytic cracking.

aromatic hydrocarbons, total ion current (TIC) data included the recording of ions at m/z 91, 105, 119, and 133 for alkylbenzenes and at m/z 128, 142, 156, 170, and 184 for naphthalenes, in addition to m/z 178, 192, 206, and 220 for phenanthrenes. Used a CR-5 ms capillary column: 30 m \times 0.25 mm ID, 0.25 μ m film thickness, with helium as the carrier gas. The temperature program was linear (100–150 °C at 12.5 °C/min; 150–310 °C at 3 °C/min), followed by an 8-min isothermal hold at 300 °C. MS conditions: 70 eV ionization energy, 270 °C ion source temperature, 50–500 Da scan range (1 scan/s, unit resolution). Hydrocarbon identification utilized NIST library and literature data.

2.3.7. SEM and EDX analysis

Analysis was performed using a Carl Zeiss Merlin FE-SEM with an Oxford Instruments AZtec X-Max EDX spectrometer (127 eV resolution). The microscope settings were a 9 mm working distance and a 20 kV accelerating voltage.

3. Results and discussion

3.1. Gas analysis

The graphical data illustrate the distribution of gaseous products generated during the aquathermolysis of heavy oil in the presence of CO₂ and various catalytic systems.

The analysis of the gas composition, presented in Fig. 3, revealed a significant dependence of the concentrations of methane (CH₄), light hydrocarbons (C₂–C₅), and hydrogen sulfide (H₂S) on the experimental conditions. The observed increase in methane concentration in certain experiments suggests the likely occurrence of the CO₂ hydrogenation reaction via the mechanism $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ [16,17], which contributes to the enrichment of the oil system with hydrogen and the subsequent formation of lighter hydrocarbon fractions. It has been experimentally established that increasing the CO₂ pressure to 40 bar (sample Ex(C40)) leads to a significant increase in the yield of hydrocarbons C₂–C₅, which is attributed to the improved solubility of CO₂ in the oil phase and the intensification of thermocatalytic cracking

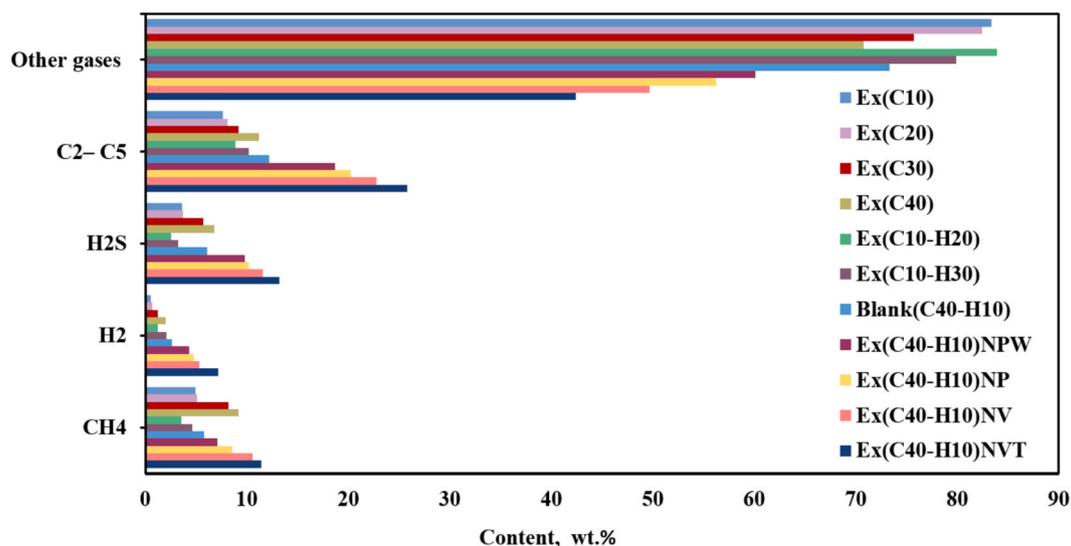


Fig. 3. Composition of the gas from the products of aquathermolysis conversion.

processes, including dehydrogenation and dealkylation reactions.

However, the introduction of the aqueous phase leads to a noticeable decrease in the concentrations of CH_4 and $\text{C}_2\text{-C}_5$, caused by a complex of factors: changes in phase equilibrium, the formation of carbonic acid (H_2CO_3) upon the dissolution of CO_2 in water, which reduces its availability for interaction with hydrocarbons, as well as the shift of the methanation reaction equilibrium to the left side: $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$ [18].

The use of catalytic systems containing acid protons (H^+) facilitates the activation of key transformations, including protonation and cracking processes, which significantly increases the yield of light hydrocarbon fractions $\text{C}_2\text{-C}_5$ [19].

3.2. Viscosity analysis

Fig. 4 demonstrates the results of experiments on non-catalytic aquathermolysis of heavy oil, emphasizing the influence of CO_2 on viscosity reduction. In the sample with water-saturated CO_2 (Blank(C40-H10)), a viscosity reduction of 59.2 % is observed compared to the original oil, while in the sample (EX(C10H30)), the reduction is 46.2 %. These differences are due to the fact that high-pressure CO_2 and low water content increase the dissolving capacity of CO_2 in heavy hydrocarbons, which is important for reducing viscosity. In the sample with non-catalytic thermolysis in the presence of CO_2 (EX(C40)), the viscosity reduction was 6.7 % compared to the control sample (Blank(C40-H10)). The interaction of CO_2 with heavy oil causes the swelling of the hydrocarbon fraction, increasing the free space between molecules and facilitating their movement, which reduces viscosity [20,21].

Fig. 5 illustrates the catalytic action of water-soluble catalysts with CO_2 on the reduction of heavy oil viscosity. It is shown that the sample Ex(C40-H10)NV, treated with Na_3VO_4 and CO_2 , demonstrates a viscosity reduction of more than 72.8 % (at 20 °C), while the sample Ex(C40-H10)NP shows a reduction of 70 % compared to heavy oil. At the same time, the combination of the catalyst Na_3VO_4 and tetralin in the sample Ex(C40-H10)NVT led to a maximum viscosity reduction of 79.5 %. Experimental data confirm that acid protons (H^+) of the catalyst effectively activate the protonation processes of hydrocarbon cracking, facilitating the formation of isomeric and hydrogenated compounds. Additionally, the introduction of tetralin as a hydrogen donor further enhances this effect, resulting in a significant reduction in the viscosity of heavy oil [12]. At the same time, CO_2 exhibits properties of a thermal cracking agent [20,22], selectively interacting with aromatic fragments, which enhances the efficiency of molecular destruction and further improves rheological properties. This synergistic effect between

catalytic and thermal actions leads to a substantial increase in the efficiency of cracking processes and an additional reduction in the viscosity of the final product.

3.3. Group compositions analysis SARA

The results presented in Fig. 6 demonstrate significant changes in the composition of heavy oil. During non-catalytic thermal decomposition under increased CO_2 pressure, a reduction in the content of resins and asphaltenes in the EX(C40) sample is observed, amounting to 19 % and 21.1 %, respectively. In the control sample with water-saturated CO_2 (Blank (C40-H10)), the decrease for resins is 15.7 %, and for asphaltenes, it is 18.4 % compared to heavy oil. These data confirm the high dissolving capacity of CO_2 , and also contribute to the swelling and loosening of intermolecular bonds, which facilitates the process of transforming high molecular weight hydrocarbons into light saturated alkanes making it an effective means for processing heavy hydrocarbons [20,23]. The introduction of catalysts such as Na_3VO_4 and tetralin into the Ex(C40-H10)NV and Ex(C40-H10)NVT samples leads to more pronounced changes in composition. The reduction in resin content was 36.2 % and 41.4 %, while asphaltenes decreased by 35.5 % and 38.2 % compared to heavy oil. These results indicate that due to the nonpolar nature of CO_2 , effective interaction occurs with polar components such as resins and asphaltenes, facilitating their breakdown and improving the cracking process [24]. Additionally, tetralin, acting as a hydrogen donor [12], significantly accelerates dehydrogenation and hydrogenation reactions when combined with the catalyst. This interaction is critically important for improving the characteristics of heavy oil [25].

3.4. Elemental composition of heavy oil

The results presented in Table 3 show significant changes in the elemental composition of heavy oil after non-catalytic and catalytic aquathermolysis. One of the main observations is the reduction in sulfur (S) content at all stages of the experiment. It is noted that under non-catalytic thermolysis conditions, there is a dependence between the decrease in sulfur content and the increase in CO_2 pressure. It is assumed that CO_2 , acting as a solvent, facilitates the mobilization of sulfur-containing compounds, breaking their bonds and converting them into more easily removable forms. In the Ex(C40) sample, the sulfur content decreased by 27.8 %, while in the Blank(C40-H10) sample, it decreased by 25.6 % compared to heavy oil. Moreover, CO_2 reduces interfacial tension and increases the availability of catalysts, which enhances the accessibility of their active sites for interaction with heavy oil fractions.

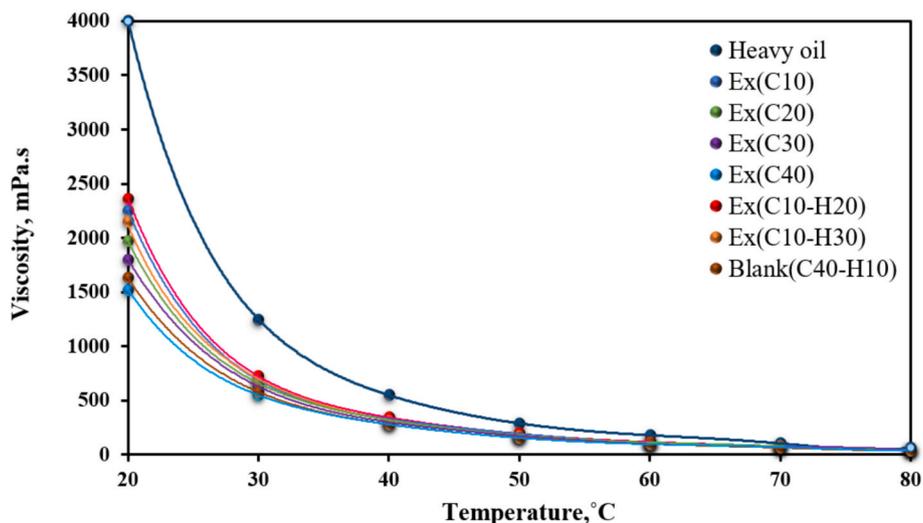


Fig. 4. Viscosity of heavy oil samples before and after non-catalytic aquathermolysis.

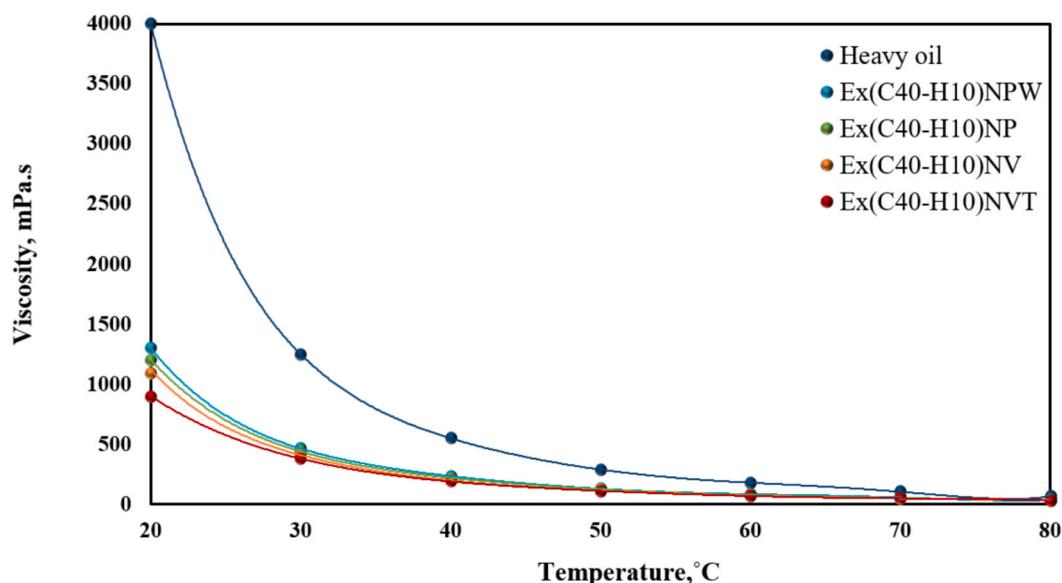


Fig. 5. Viscosity of heavy oil samples before and after catalytic upgrading.

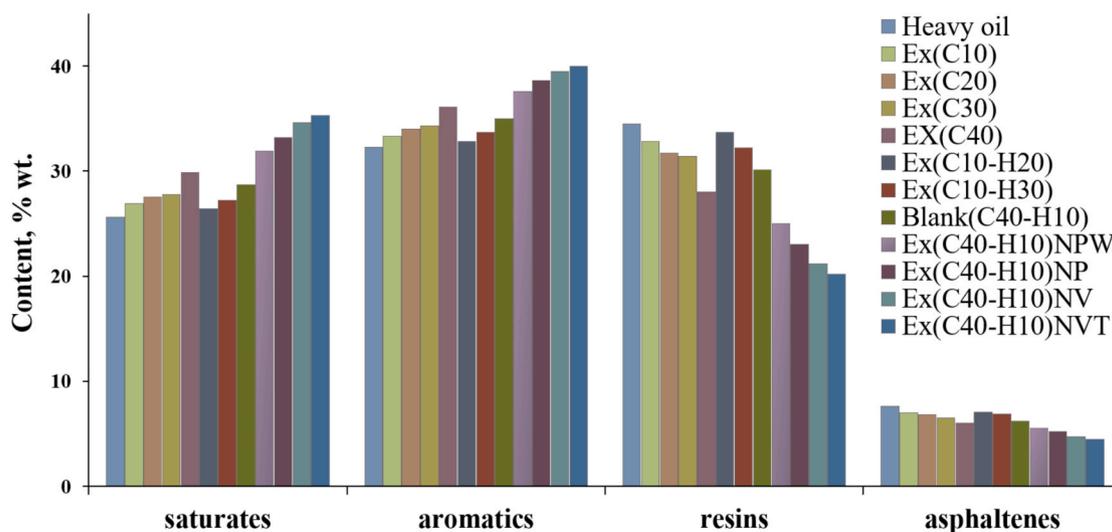


Fig. 6. Group composition of heavy oil samples before and after non-catalytic and catalytic aquathermolysis.

Table 3
Elemental composition of heavy oil samples before and after aquathermolysis.

Samples	Elemental content (wt.%)					
	C	H	S	N	O	H/C
Heavy oil	81.98	11.12	5.54	0.38	0.98	1.63
Ex(C10)	82.43	12.1	4.28	0.3	0.89	1.76
Ex(C20)	82.4	12.32	4.2	0.25	0.83	1.79
Ex(C30)	82.42	12.35	4.19	0.24	0.8	1.80
Ex(C40)	82.44	12.68	4.0	0.2	0.68	1.85
Ex(C10-H20)	82.41	11.94	4.4	0.34	0.91	1.74
Ex(C10-H30)	82.39	12.25	4.23	0.28	0.85	1.78
Blank(C40-H10)	82.32	12.6	4.12	0.21	0.75	1.84
Ex(C40-H10)NPW	82.77	12.84	3.56	0.18	0.65	1.86
Ex(C40-H10)NP	82.85	12.93	3.45	0.17	0.6	1.87
Ex(C40-H10)NV	82.92	13.1	3.25	0.15	0.58	1.90
Ex(C40-H10)NVT	82.96	13.32	3.10	0.11	0.51	1.93

Experimental studies of samples Ex(C40-H10)NV and Ex(C40-H10)NP, containing catalysts Na_3VO_4 and NaH_2PO_4 , respectively, demonstrated a significant reduction in sulfur content by 41.7 % and 37.7 % compared

to the original heavy oil. The maximum degree of desulfurization (44 %) was achieved with the introduction of tetralin as a hydrogen donor in combination with the catalytic system Na_3VO_4 (sample Ex(C40-H10)NVT), confirming the synergistic effect between catalytic activation and the hydrogen-donating ability of the medium. It was established that in the presence of catalysts possessing acidic protons (H^+), key acid-catalytic processes occur, including protonation, cracking, isomerization, and dehydration. Proton attack activates high molecular weight hydrocarbon molecules, facilitating the breaking of C-S bonds in sulfur-containing organic compounds, resulting in the subsequent release of sulfur in gaseous form (H_2S) or as soluble sulfides [26,27]. The removal of sulfur-containing components and the conversion of heavy fractions into lighter hydrocarbons with increased hydrogen content lead to a significant increase in the H/C ratio in the modified oil [28,29]. The high hydrogen content in the obtained products enhances their quality characteristics and increases the energy value of the processed products.

3.5. Comparison with literary data

Table 4 presents a comparative analysis of the results from various

Table 4Comparison of the influence of catalysts and conditions on the upgrading of heavy oil in CO₂: Our research and literature data.

Catalyst type	Hydrogen donor	Reaction conditions		S wt. %	Viscosity reduction, mpa. s 20 °C, %	Asphaltenes	Ref.
		Temperature, Pressure, Time	Oil: Water				
Our results							
Feedstock	—	—	—	5.4	4000	7.6	
Without catalyst-CO ₂	—	300 °C, CO ₂ 40 bar, 24 h.	50:10	25.6	59.2	6.2	
Na ₂ H ₅ P(W ₂ O ₇) ₆	—	300 °C, CO ₂ 40 bar, 24 h.	50:10	35.7	67.5	5.5	
NaH ₂ PO ₄	—	300 °C, CO ₂ 40 bar, 24 h.	50:10	37.7	70	5.2	
Na ₃ VO ₄	—	300 °C, CO ₂ 40 bar, 24 h.	50:10	41.3	72.8	4.7	
Na ₃ VO ₄	Tetralin	300 °C, CO ₂ 40 bar, 24 h.	50:10	44	79.5	4.5	
Other studies							
Feedstock	—	—	—	5.85	2676	6.75	[30]
Without catalyst	—	300 °C, CO ₂ 10 bar, 24 h.	70:30	18.6	43	7.6	[30]
Na-Fe catalyst	—	300 °C, CO ₂ 10 bar, 24 h.	70:30	25.1	61	6.75	[30]
Feedstock	—	—	—	—	3309	—	[31]
Without catalyst-CO ₂	—	300 °C, CO ₂ 10 bar, 48 h.	70:30	—	46.4	—	[31]
Nickel tallate catalyst	Dissolved in a hydrogen-donating (white spirit)	300 °C, CO ₂ 10 bar, 48 h.	70:30	—	64.7	12.5	[31]
Feedstock	—	—	—	—	3368	5.37	[32]
Without catalyst-CO ₂	—	300 °C, CO ₂ 15 bar, 5 h.	70:30	—	22.2	5.93	[32]
Fe, CO, Cu, catalyst	Tetralin	300 °C, CO ₂ 15 bar, 5 h.	70:30	—	43.5	5.69	[32]
Fe, CO, Cu, catalyst	Propanol	300 °C, CO ₂ 15 bar, 5 h.	70:30	—	44.8	6.31	[32]

studies on the processing of heavy oil under aquathermolysis conditions in a CO₂ environment. It examines reactions without a catalyst, as well as those using water-soluble and oil-soluble catalysts. The focus is on the impact of experimental conditions, such as the water/oil ratio and the partial pressure of CO₂, on the effectiveness of viscosity reduction, sulfur content, and asphaltenes. It is emphasized that the high efficiency of water-soluble catalysts is achieved through a combination of high CO₂ pressure and an optimal oil/water ratio (50:10), which surpasses the results of other studies with a 70:30 ratio at lower CO₂ pressures. A higher water content decreases the concentration of CO₂ in the oil phase, negatively affecting viscosity reduction. Optimal CO₂ pressure and component ratios enhance the interaction of the catalyst with the reagents, facilitating a deeper transformation of heavy oil components. The effectiveness of the catalysts depends on the composition of the raw materials, their nature, and the reaction conditions. However, comparing the results of different studies is complicated due to variations in experimental conditions, highlighting the need for further research to determine the optimal conditions for aquathermolysis and the selection of effective catalytic systems.

3.6. Analysis of IR spectra

The IR spectra shown in Fig. 7a were obtained in the range from 400 to 4000 cm⁻¹ for heavy oil (a) and asphaltenes (b) before and after catalytic aquathermolysis. The observed shifts and changes in intensity highlight the effectiveness of this process in improving the quality of heavy oil through hydrogenation and modification of the hydrocarbon composition.

Table 5 presents the studied samples of the product obtained as a result of aquathermolysis under the influence of CO₂ and a water-soluble catalyst. During this process, long aliphatic hydrocarbon chains decompose, and their monomers and oligomers are broken down into shorter fragments. These fragments can recombine to form aromatic compounds, leading to an increase in their concentration in the system. This transformation not only changes the composition of the product but also affects the intensity of the absorption bands in the IR spectra, as the

molecules of aromatic compounds have characteristic spectroscopic properties. Furthermore, in the products of aquathermolysis conversion, there is a decrease in the content of sulfonic groups (RSO₃H/C=C) and sulfide bonds (S-O/C=C) compared to the original heavy oil. This decrease can be explained by the pyrolysis of carbon dioxide (CO₂), which reacts with the sulfides (R-S-R) contained in the oil. During these reactions, less reactive sulfoxides (R-S(=O)-R) and sulfonic acids (R-SO₂-R) are formed [20]. These products have lower reactivity and can be effectively removed from heavy oil, potentially improving the quality of the final product.

3.7. Nuclear magnetic resonance

The 1H NMR spectra examined heavy oil before and after aquathermolysis. The distribution of hydrogen atom types includes: H_A-aromatic hydrogen (9.0–6.0 ppm), H_α-aliphatic hydrogen on C_α, adjacent to aromatic rings (4.0–2.0 ppm), H_β-aliphatic hydrogen on C_β and CH₂, as well as CH for C_β near aromatic rings (2.0–1.0 ppm), and H_γ-aliphatic hydrogen on C_γ and CH₃ for C_γ, which is adjacent to aromatic rings (1.0–0.5 ppm). This classification was achieved using chemical shifts and integral areas. Furthermore, structural parameters of the aromatic hydrocarbons were calculated, including aromaticity (f_A), condensation aromaticity (HAU/CA), branching index (BI), and conversion rate in aromatic rings (σ), employing enhanced methods developed by Brown-Ladner [33,34].

Table 6 shows the changes in f_A, HAU/CA, BI, and σ for the samples both before and after the reaction

In Table 6, the samples obtained after aquathermolysis show a decrease in the level of aromaticity (f_A) and the branching index (BI), as well as an increase in the condensation coefficient of aromaticity (HAU/CA). These changes indicate the transformation of aromatic compounds into less aromatic or aliphatic structures, which, in turn, contributes to the formation of more stable aromatic compounds with a low tendency for further decomposition. The decrease in the branching index also indicates dehydrogenation and dealkylation processes, which lead to the removal of side alkyl chains from hydrocarbon molecules and,

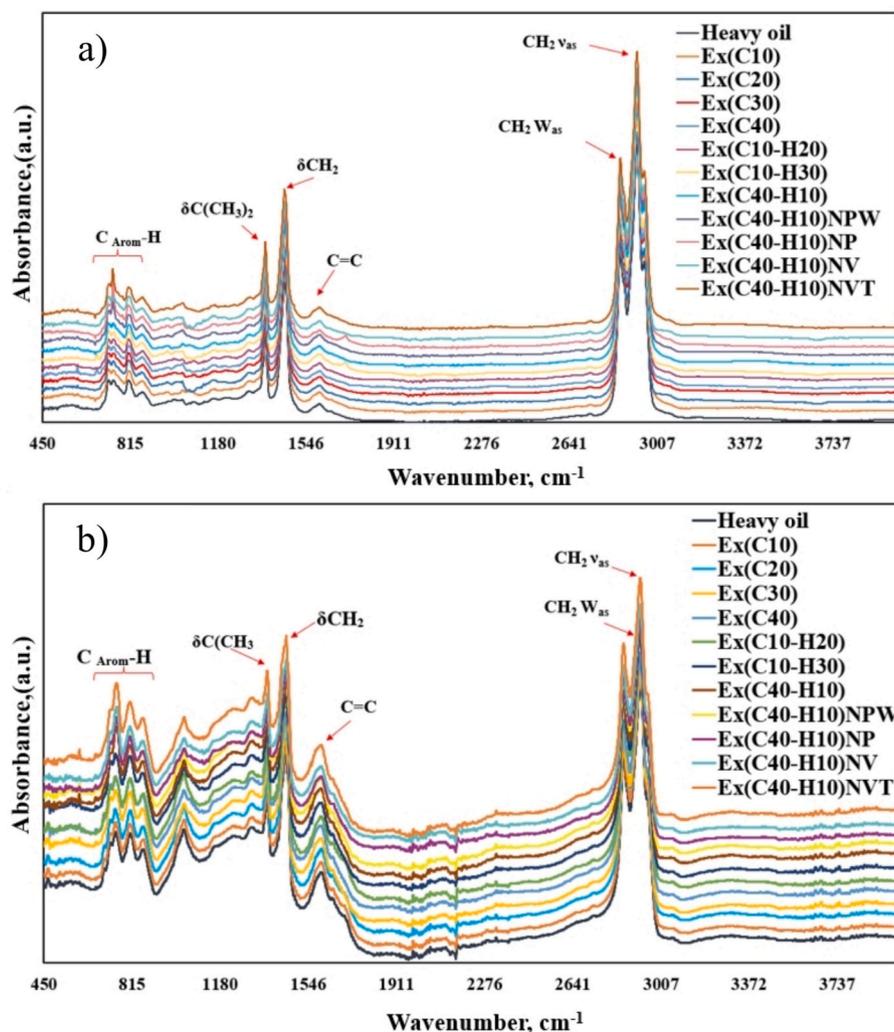


Fig. 7a. IR spectra of heavy oil and catalytic aquathermolysis in the presence of a catalyst.

consequently, to a reduction in the number of branches in their structure [20,34]. This change in the composition and structure of hydrocarbons indicates that aquathermolysis not only transforms hydrocarbons but also improves the stability of the resulting compounds, making them more resistant [35].

3.8. Analysis of GC-MS spectra

Chromatographic analysis of the fractions of normal hydrocarbons obtained from the aquathermolysis of heavy oil shows changes in their composition (Fig. 7b). The leftward shift of the peaks indicates an increase in low-molecular n-alkanes and iso-alkanes, which is associated with the cracking of long-chain alkanes. The use of water-soluble catalysts and CO₂ enhances the destruction of resins and asphaltenes, as well as increases the intensity of the n-alkane peaks with retention times of less than 10 min. In the later stages of the analysis, clear peaks are maintained, which may indicate the stabilization of the hydrocarbon composition and the completion of degradation processes.

The presented Fig. 8 shows that the observed changes indicate an increase in the content of alkanes and a decrease in the number of hopanes and cycloalkanes, reflecting the processes of hydrocarbon transformation. Under non-catalytic conditions, CO₂, with increasing pressure in the samples EX(C40) and EX(C40H10), enhances the breaking of bonds in complex hydrocarbons, facilitating the formation of simpler alkanes through interaction with the polar centers of organic compounds. The process of CO₂ dissolution causes the swelling of

hydrocarbons and loosens intermolecular bonds, leading to the dehydration and transformation of asphaltenes and resins into lighter saturated and aromatic hydrocarbons. Under catalytic conditions, the use of water-soluble sodium-based catalysts with an acidic proton significantly accelerates chemical reactions and promotes effective bond breaking, including dehydrogenation and hydrogenation reactions [36]. During these processes, hydrogen atoms attach to unsaturated hydrocarbons, resulting in their saturation and the formation of alkanes [37]. This observation, combined with the results of SARA analysis (Fig. 6), confirms the destructive hydrogenation of high-molecular alkyl radicals from resins and asphaltenes.

Chromatographic analysis of the total ion current (TIC) of the aromatic fraction of heavy oil subjected to aquathermolysis (Fig. 9) shows significant changes in composition under catalytic treatment. At the initial stages, peaks of alkylbenzenes (C10-C13) and tetralins are recorded up to the eighth minute of analysis. The introduction of a catalyst with CO₂ leads to a decrease in the intensity of these peaks and the appearance of new ones, indicating changes in aromatic hydrocarbons, particularly low-boiling compounds. At later stages, a significant decrease in peak intensity is observed, which may indicate a deep transformation of the initial compounds. At the same time, in a CO₂ environment and using water-soluble catalysts, a greater variety of peaks is recorded compared to the non-catalytic process, which may indicate more complex reaction processes occurring under catalytic reaction conditions.

Fig. 10 demonstrates that increasing CO₂ pressure enhances its

Table 5
Spectral coefficients of heavy oil samples based on FTIR spectra.

Samples	CH ₂ /C=C	C=C/CH ₃ + CH ₂	CH ₃ /CH ₂	C=C/CH ₃	R-C=O/C=C	RSO ₃ H/C=C
Oil						
Heavy oil	8.10	0.15	1.80	0.27	0.43	1.31
Ex(C10)	6.94	0.17	1.83	0.25	0.39	1.28
Ex(C20)	7.58	0.21	1.86	0.23	0.36	1.25
Ex(C30)	7.60	0.23	1.87	0.22	0.34	1.22
EX(C40)	7.68	0.26	1.9	0.19	0.32	1.17
Ex(C10-H20)	6.82	0.16	1.81	0.26	0.41	1.3
Ex(C10-H30)	7.16	0.19	1.84	0.24	0.38	1.27
Blank(C40-H10)	7.64	0.24	1.89	0.20	0.33	1.19
Ex(C40-H10)NPW	7.78	0.28	1.92	0.16	0.30	1.15
Ex(C40-H10)NP	7.79	0.29	1.93	0.15	0.28	1.14
Ex(C40-H10)NV	7.81	0.30	1.95	0.14	0.27	1.12
Ex(C40-H10)NVT	7.86	0.32	1.98	0.12	0.26	1.1
Asphaltenes						
Heavy oil	1.38	0.37	1.2	0.44	1.71	1.28
Ex(C10)	1.19	0.4	1.22	0.40	1.67	1.26
Ex(C20)	1.23	0.43	1.25	0.37	1.62	1.21
Ex(C30)	1.25	0.45	1.27	0.35	1.60	1.2
EX(C40)	1.28	0.48	1.31	0.32	1.56	1.17
Ex(C10-H20)	1.15	0.39	1.21	0.43	1.69	1.27
Ex(C10-H30)	1.20	0.42	1.24	0.38	1.65	1.24
Blank(C40-H10)	1.27	0.47	1.29	0.33	1.58	1.19
Ex(C40-H10)NPW	1.31	0.52	1.33	0.30	1.51	1.16
Ex(C40-H10)NP	1.32	0.55	1.36	0.28	1.49	1.15
Ex(C40-H10)NV	1.35	0.57	1.37	0.26	1.42	1.13
Ex(C40-H10)NVT	1.36	0.60	1.39	0.24	1.39	1.12

(CH₂/C=C) = D1450/D1600, aliphaticity. (C=C/CH₃ + CH₂) = D1600/D720, aromaticity. (CH₃/CH₂) = D1380/D720, branching. (C=C/CH₃) = D1600/D740, degree of condensation. (R-C=O/C=C) = D1700/D1600, degree of oxidation. (RSO₃H/C=C) = D1030/D1600, degree of (sulfurization – sulfonates).

Table 6
H-NMR analysis of heavy oil before and after aquathermolysis.

Samples	H _A , %	H _{ar} , %	H _β , %	H _γ , %	f _A	H _{AU} /C _A	BI	σ
Heavy oil	16.95	13.28	41.81	27.96	0.324	1.185	0.338	0.281
Ex(C10)	14.67	13.52	43.27	28.54	0.248	1.519	0.335	0.315
Ex(C20)	12.22	13.99	44.92	28.87	0.213	1.622	0.327	0.364
Ex(C30)	11.58	14.11	45.21	29.10	0.205	1.634	0.327	0.379
EX(C40)	9.98	14.47	45.67	29.88	0.169	1.877	0.331	0.420
Ex(C10-H20)	15.38	13.63	42.96	28.03	0.264	1.460	0.330	0.307
Ex(C10-H30)	14.20	13.63	43.50	28.67	0.235	1.598	0.335	0.324
Blank(C40-H10)	10.85	14.23	45.30	29.62	0.181	1.820	0.332	0.396
Ex(C40-H10)NPW	9.14	14.59	46.01	30.26	0.154	1.983	0.333	0.444
Ex(C40-H10)NP	8.79	14.62	46.12	30.47	0.146	2.066	0.334	0.454
Ex(C40-H10)NV	8.52	14.72	46.25	30.51	0.132	2.277	0.334	0.463
Ex(C40-H10)NVT	7.36	15.19	46.56	30.89	0.113	2.537	0.333	0.508

extraction capacity. CO₂ molecules possess a high ability for intermolecular interactions due to the presence of π-electrons in their electron shells, which is similar to the properties of aromatic hydrocarbons. This leads to an increase in the aromaticity of hydrocarbons through the destruction of complex aromatic compounds and the formation of lighter hydrocarbons, such as alkylbenzenes and naphthalenes [11,38]. Additionally, CO₂ reduces the interfacial tension at the oil–water interface, which increases the availability of water-soluble catalysts and accelerates catalytic reactions of hydrocracking and hydrodesulfurization of heavy aromatic compounds (such as phenanthrenes, benzothiophenes, dibenzo- and naphthothiophenes). The hydrocracking process results in the fragmentation of complex structures, creating lighter molecules, while hydrodesulfurization removes sulfur from heterocyclic compounds, thereby reducing its concentration in the sample. These processes are confirmed by IR spectroscopy data, which show a decrease in the content of RSO₃H/C=C, as well as results from elemental composition analysis indicating a reduction in sulfur content. As a result, there is an increase in the proportion of alkylbenzenes and naphthalenes, along with a simultaneous decrease in the content of polycyclic aromatic hydrocarbons and thiophenes in the aromatic fraction of oil. The resulting lighter aromatic compounds are stabilized during the reaction processes.

3.9. SEM and EDX analysis

SEM microphotographs (Fig. 11) demonstrate differences in the morphology of solid particles formed during the aquathermolysis of heavy oil in the presence of catalysts (A) Na₂H₅P(W₂O₇)₆, (B) NaH₂PO₄, and (C) Na₃VO₄, reflecting the influence of catalysts on aquathermolysis processes. From image A, it can be observed that the surface structure consists of dense particles forming large agglomerates. The high content of carbon and tungsten indicates a carbon matrix, possibly reinforced with tungsten. Image B shows a more varied grain structure compared to A. Distinct rounded particles and porous inclusions are observed, with a high content of oxygen and phosphorus. Image C is characterized by a fine-grained and porous structure. These particles, compared to A and B, are more dispersed and have a smaller size. This structure indicates high dispersity and the presence of many small pores. Based on these images and elemental analysis, it can be concluded that each sample has its specific microstructure and chemical composition, which can significantly affect their physicochemical properties and potential applications.

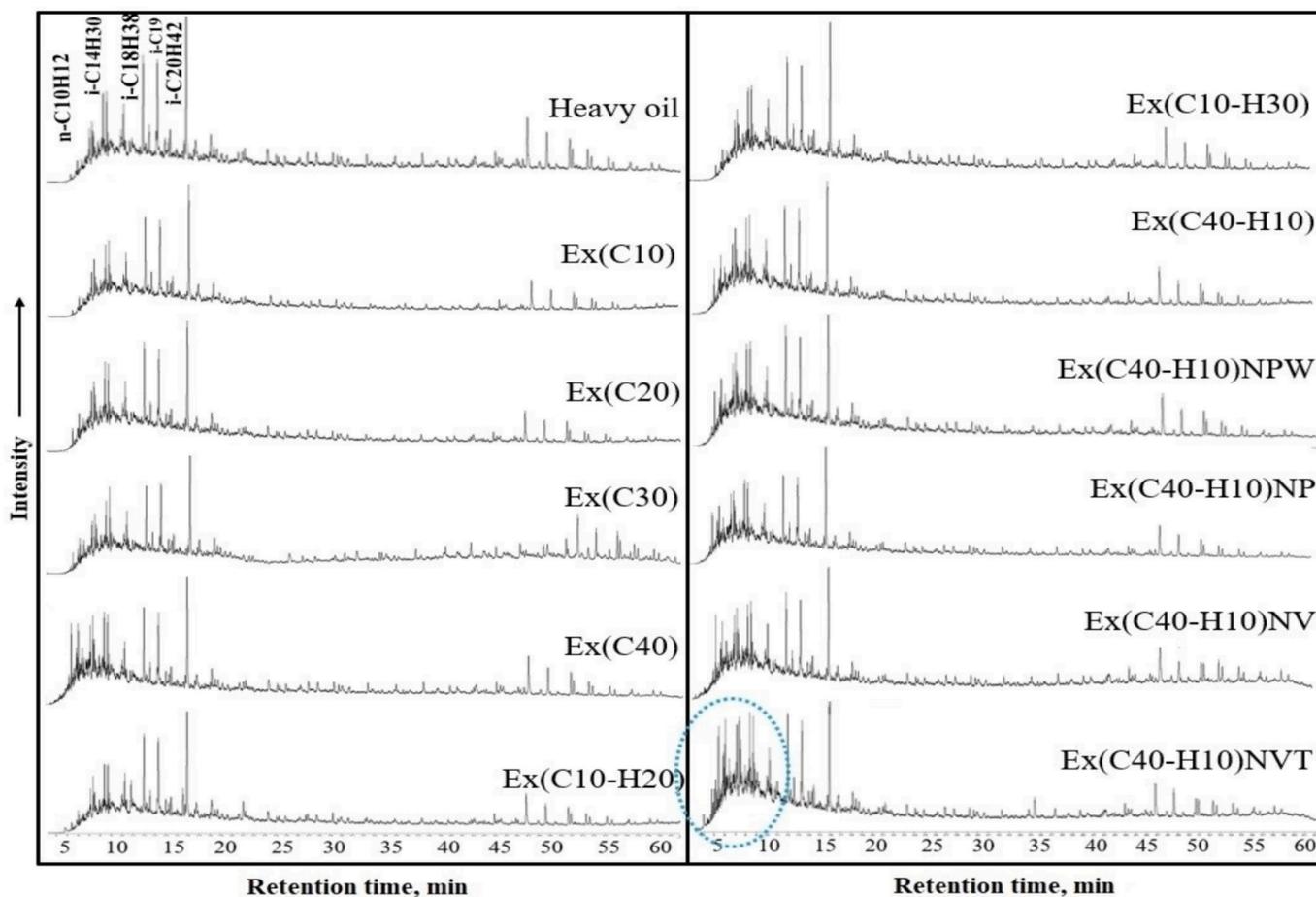


Fig. 7b. The GC-MS spectra of saturated hydrocarbons before and after catalytic thermolysis.

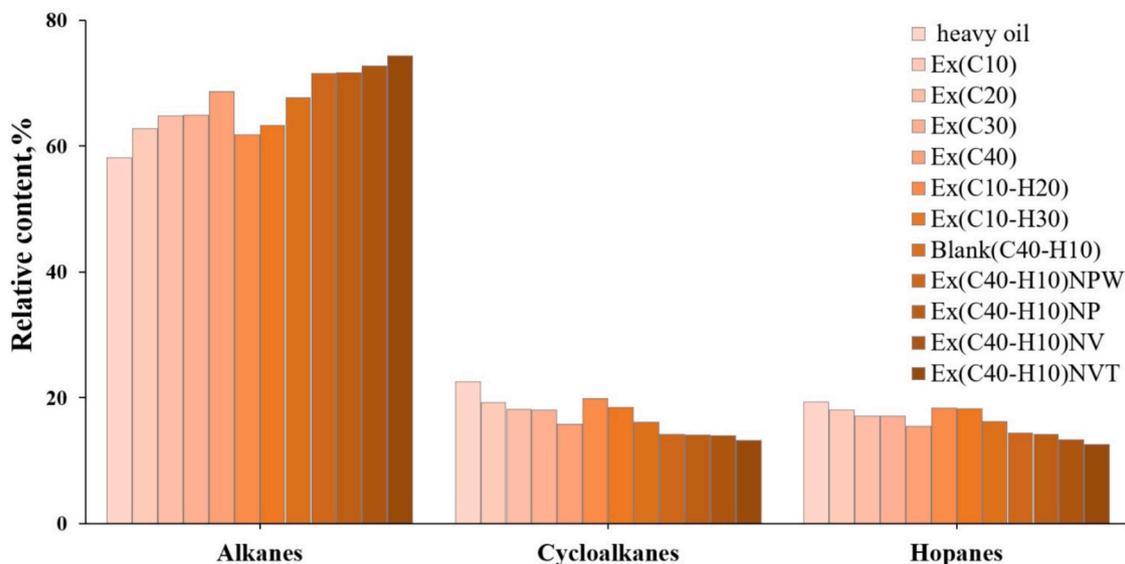


Fig. 8. GC-MS analysis of saturated hydrocarbons: alkanes, cycloalkanes, hopanes.

3.10. Mechanisms and reactions of CO₂-assisted heavy oil upgrading

Fig. 12 schematically presents the mechanisms of catalytic aquathermolysis of heavy oil in the presence of CO₂, as well as the key role of the catalysts Na₂H₅P(W₂O₇)₆, NaH₂PO₄, and Na₃VO₄ in this process.

The mechanism for the enrichment of heavy oil using carbon dioxide (CO₂) under high pressure and temperature, catalyzed by water-soluble catalysts, includes several key stages:

1-CO₂ as a heat carrier and soluble component

Under high pressure, carbon dioxide penetrates the structure of

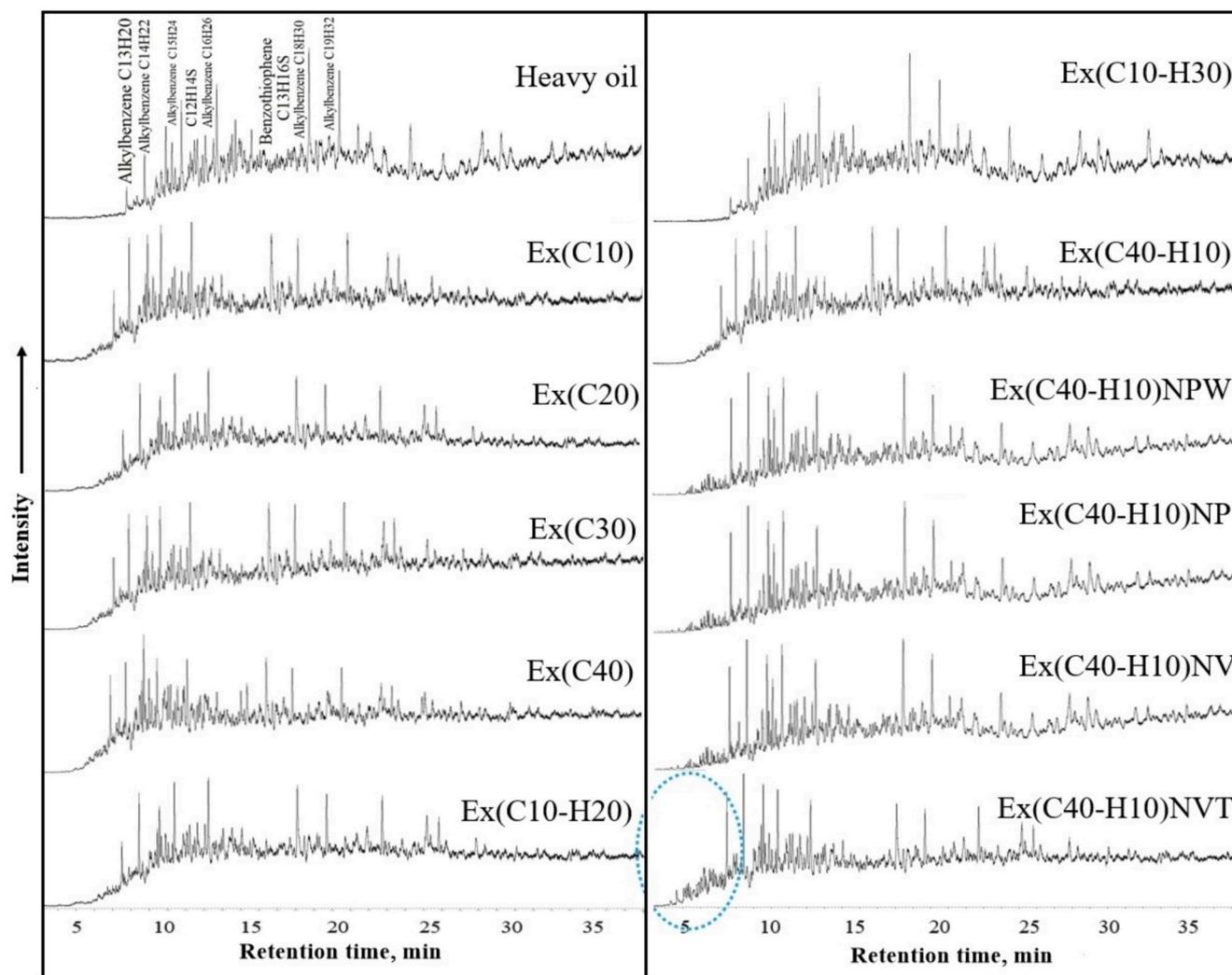


Fig. 9. The GC-MS spectra (TIC) of aromatics hydrocarbon fractions before and after catalytic thermolysis.

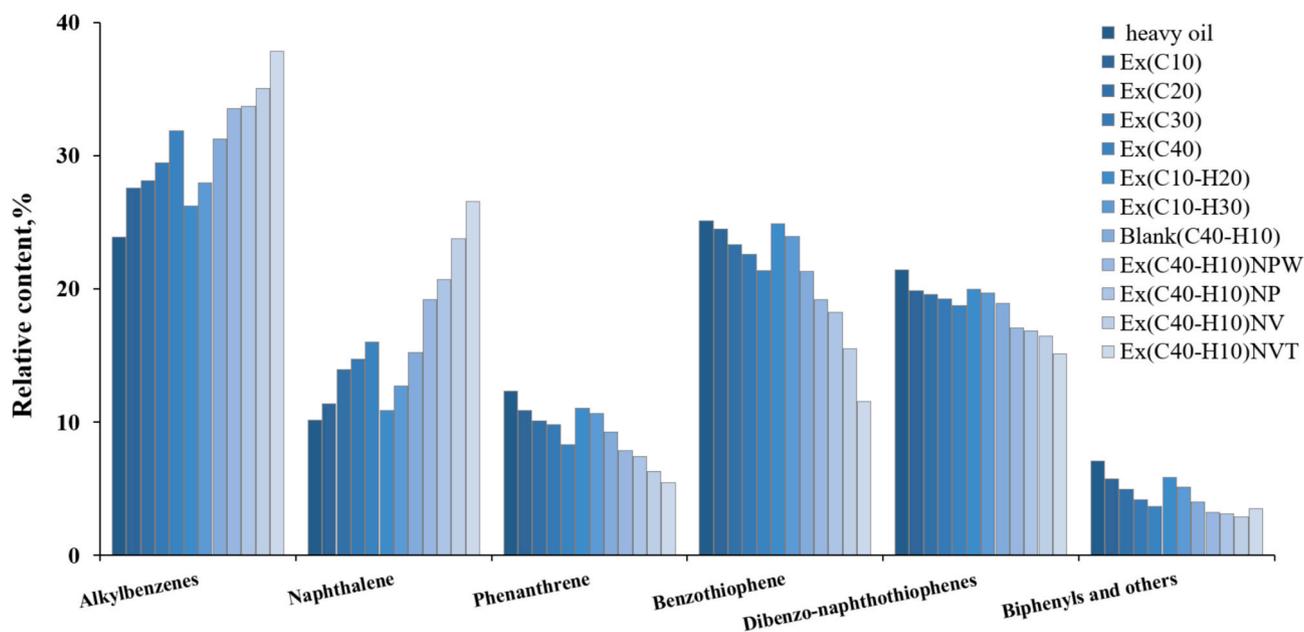


Fig. 10. Proportional composition of aromatic compounds within the aromatic fractions.

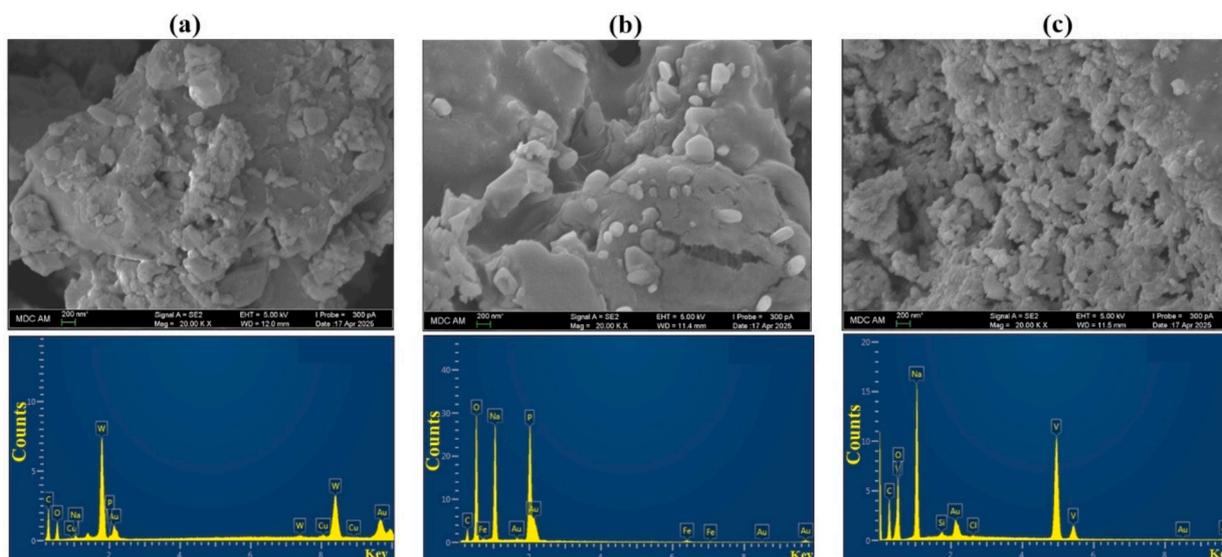


Fig. 11. SEM images (a, b, c) of particle sizes and EDX analysis of catalysts after aquathermolysis.

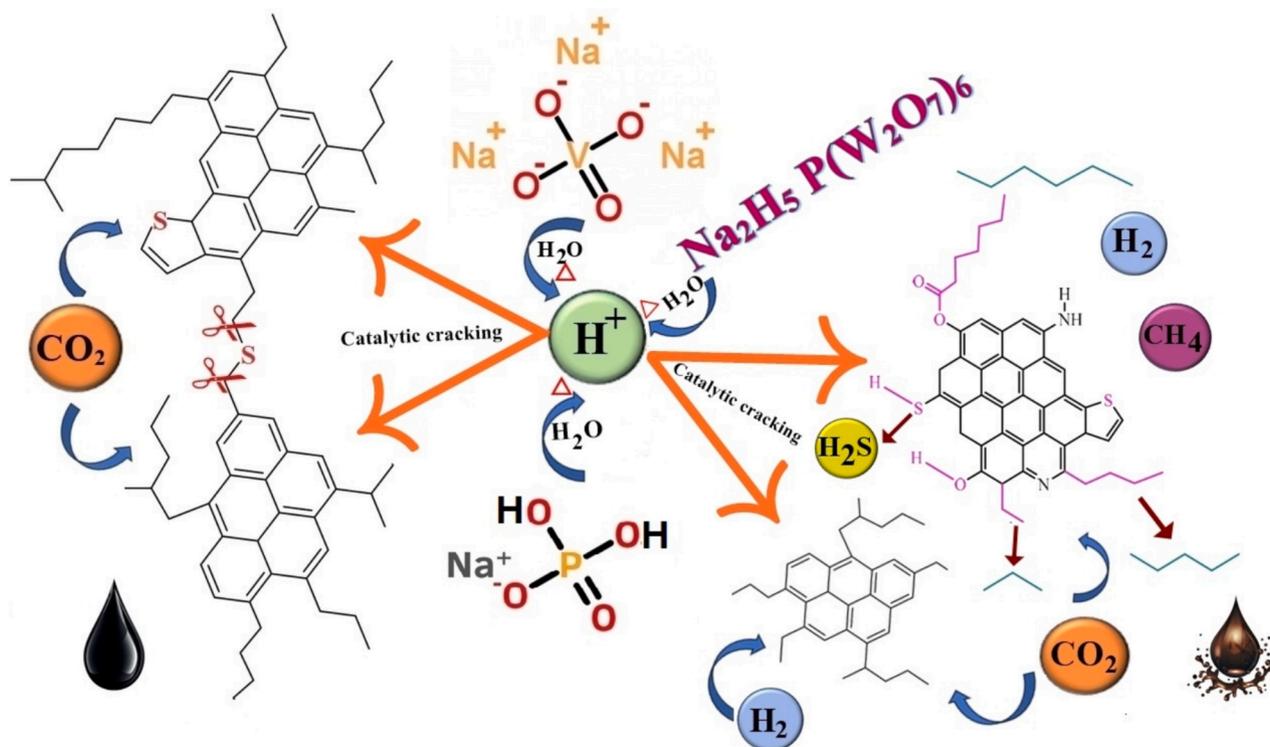


Fig. 12. Schematic of the mechanism of catalytic aquathermolysis of heavy oil in a CO_2 atmosphere.

heavy hydrocarbons, acting as a solvent and heat carrier, which enhances the oil's flowability [20,23,39]. Experimental results show a significant reduction in the viscosity of heavy oil with increasing CO_2 pressure, confirming its impact on improving flowability.

2. Swelling and dehydration

CO_2 causes the swelling of hydrocarbons and loosens intermolecular bonds [20,23,39], leading to dehydration and the transformation of asphaltenes and resins into lighter saturated and aromatic hydrocarbons. These processes are supported by the results of sara-analysis, which show an increase in the proportion of alkanes in saturated chromatography (GC-MS) samples.

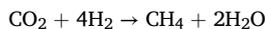
3. CO_2 as a thermal cracking Agent [20,22,40]

Molecules of CO_2 exhibit a pronounced ability for intermolecular interactions due to the presence of π -electron clouds in their electronic structure, similar to aromatic hydrocarbons. This property leads to an increase in the aromaticity of hydrocarbon systems, which is quantitatively confirmed by the rise in the aromaticity coefficient ($\text{C}=\text{C}/\text{CH}_3+\text{CH}_2$) in IR spectra and the increase in the aromatic condensation coefficient (HAU/CA) in proton ^1H NMR spectra. Concurrently, there is an observed increase in the share of alkylbenzenes in the aromatic fraction when analyzed by GC-MS, accompanied by a decrease in the content of benzo-thiophene structures, resulting in a reduction of the overall sulfur content in the system. These structural changes are corroborated by IR spectroscopy data through the dynamics of the

coefficient ($\text{RSO}_3\text{H}/\text{C}=\text{C}$), as well as by the results of elemental sulfur (S) analysis, demonstrating the complex influence of CO_2 on the modification of hydrocarbon composition and the desulfurization of oil fractions.

4. Hydrogenation and formation of light hydrocarbons

CO_2 can react with hydrogen to produce water and methane: [20,41].

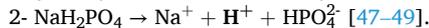
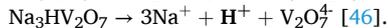
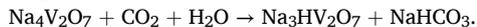
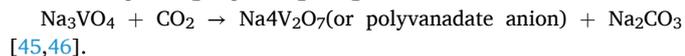
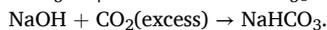


This interaction leads to an increase in the content of light hydrocarbons and the H/C ratio in heavy oil. Additionally, the interaction of CO_2 with water results in the formation of carbonic acid ($\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$), which dissociates into hydrogen ions and bicarbonate ($\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$) [20,42]. These ions promote carbocation mechanisms, increasing the share of isomers, reducing viscosity, and enhancing the H/C ratio.

5. Reduction of Interfacial Tension

CO_2 reduces the interfacial tension at the oil–water interface [20,43], increasing the availability of reactive components and enhancing the interaction between oil and the water-soluble sodium-based catalyst (NaH_2PO_4 and $\text{Na}_2\text{H}_5\text{P}(\text{W}_2\text{O}_7)_6$). This catalyst, possessing an acidic proton, intensifies the oxidative-dehydrogenation reactions of naphthenes and cycloalkanes [36], facilitating the formation of hydrogen protons in the system and the progression of hydrogenation and isomerization reactions [20,44]. A water-soluble catalyst, such as Na_3VO_4 , interacts with CO_2 to form a polymeric vanadate anion, which also contains an acidic proton.

–The interaction processes can be described by the following reactions:



4. Conclusions

The results of our study indicate a significant potential for the use of carbon dioxide and water-soluble catalysts to improve the efficiency of heavy oil processing.

- In the process of thermal cracking of heavy oil, increasing the pressure of CO_2 enhances its solubility and swelling in heavy hydrocarbons, which reduces viscosity.
- High CO_2 pressure and low water levels during aquathermolysis contribute to an increase in the dissolving capacity of CO_2 in heavy hydrocarbons compared to low CO_2 pressure and high water content.
- The use of water-soluble sodium-based catalysts with an acidic proton significantly accelerates key dehydrogenation, hydrogenation, and isomerization reactions, minimizes side processes, and ensures a deeper transformation of oil components.
- Experimental data showed that the combination of catalysts Na_3VO_4 and NaH_2PO_4 with CO_2 reduces the viscosity of heavy oil by 72.8 % and 70 %, respectively, and also leads to a reduction in sulfur content by 41.7 % and 37.7 % compared to the original heavy oil.
- The combination of the catalyst Na_3VO_4 with tetralin under CO_2 pressure enhances the effect of viscosity reduction by 79.5 %, the content of asphaltenes by 38.2 %, and sulfur by 44 % compared to the original heavy oil.

These results underscore the need for further research in CO_2 -based

hydrocarbon processing technologies and water-soluble catalysts, opening new horizons for the development of more efficient methods for the extraction and processing of complex hydrocarbon resources.

CRedit authorship contribution statement

Yasser I.I. Abdelsalam: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Lilia Kh. Galiakhmetova:** Validation. **Vladimir E. Katnov:** Validation. **Irek I. Mukhamatdinov:** Validation. **Rustam R. Davletshin:** Validation. **Alexey V. Vakhin:** Funding acquisition, Resources.

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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.

Data availability

No data was used for the research described in the article.

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