International Journal of Advanced Research and Development
www.multireviewjournal.com
ISSN: 2455-4030
Received: 15-11-2025, Accepted: 10-01-2026, Published: 27-01-2026
Volume 11, Issue 1, 2026, Page No. 29-32

Effect of an additional component on the chemical composition of heavy petroleum residues

Soltan Aliyev[1], Zulfiyya Chalabizada[2]
[1]Associate Professor, Department of Petrochemical Technology and Industrial Ecology, Azerbaijan State Oil and Industry University, Azerbaijan
[2] Department of Petrochemical Technology and Industrial Ecology, Azerbaijan State Oil and Industry University, Azerbaijan

Abstract
The main characteristic of heavy petroleum feedstock is the high content of resin–asphaltene components, which are prone to coke formation and complicate processing by catalytic methods. Therefore, the development of effective, low-cost redox-active initiator additives for the upgrading of heavy hydrocarbon feedstocks remains a significant technological challenge.
In this study, heavy paraffinic fuel oil was used as the feedstock, while ferrospheres (FS) derived from thermal power plant (TPP) ash were applied as a redox-active initiator additive. The effect of ferrospheres on the yield of fuel fractions (boiling point ≤ 360 °C) and on the transformation of resin–asphaltene components during thermal cracking was investigated.
The results show that the addition of ferrospheres does not lead to a noticeable increase in the yield of fuel fractions; however, it leads to a reduction of the total resin–asphaltene content by approximately 50%. At temperatures of 400–450 °C, the oil fraction yield increases by 5.9–6.7 mass % due to intensified resin decomposition, while at 500 °C it promotes deeper conversion of heavy components, resulting in enhanced formation of gas and solid products. The observed activity of ferrospheres is attributed to the redox properties of hematite and the selective adsorption of resin–asphaltene components on iron oxide surfaces.
Overall, the obtained results confirm the potential of ferrospheres as an effective and low-cost initiator additive for regulating the transformation of heavy petroleum residues.

Keywords: Thermal cracking, fuel oil, resins, asphaltenes, ferrospheres, initiator additive

Introduction

The steady depletion of light and medium crude oil reserves has led to an increased utilization of heavy crude oils in refinery feedstocks. Heavy crude oils are characterized by a high content of resin–asphaltene components, whose molecules are characterized by large molecular sizes, complex polyaromatic structures, and a significant amount of heteroatoms. These features lead to increased viscosity and density of heavy crude oils and determine their pronounced tendency toward aggregation and coke formation during thermal and catalytic processing [1-5].
The presence of resin–asphaltene components significantly complicates the processing of heavy hydrocarbon feedstocks by conventional catalytic methods. During thermal treatment, these components readily undergo condensation and polymerization reactions, leading to the formation of coke and solid by-products, which negatively affect process efficiency and equipment operation. Therefore, the development of new approaches for controlling the transformation pathways of resin–asphaltene components remains an important scientific and technological task [6-8].
In recent years, considerable attention has been paid to the study of the structural features of high-molecular-weight petroleum components and their transformation behavior under thermal and thermocatalytic conditions. Numerous studies have shown that the stability of heavy petroleum systems is largely governed by the interactions between resins and asphaltenes, which determine their colloidal structure and resistance to thermal destruction. Disruption of these interactions can facilitate the breakdown of resin–asphaltene aggregates and suppress undesirable coke formation [9-11].
One of the promising approaches to reducing the cost of petroleum upgrading processes is the involvement of secondary raw materials and industrial waste as functional additives. The literature reports the use of plastics, rubber waste, biomass, and other materials as co-processing components or initiator additives. In this context, ferrospheres (FS) derived from thermal power plant (TPP) ash are of particular interest as low-cost redox-active materials. These materials are rich in iron oxides that actively participate in oxidation–reduction reactions and influence hydrocarbon conversion pathways [12].
Ferrospheres are readily available, inexpensive, and significantly cheaper than conventional heterogeneous catalysts. In addition, their utilization contributes to the partial solution of the problem of TPP ash disposal. Previous studies have demonstrated that iron-containing additives can promote the destruction of resin–asphaltene components during the processing of heavy petroleum feedstocks [13-15].
The present work investigates the effect of ferrosphere-based redox-active initiator additives on the material and fractional composition of products obtained during the thermal cracking of heavy paraffinic fuel oil, with particular attention paid to the transformation of resin–asphaltene components.

Experimental Part

The object of the study was a petroleum residue obtained after atmospheric distillation of heavy paraffinic crude oil at temperatures above 350 °C. The residue is characterized by a high content of resin components and a relatively low

content of asphaltenes, which makes it a suitable model feedstock for studying the transformation of resin–asphaltene systems under thermal cracking conditions.

Ferrospheres separated from the ash of a thermal power plant were used as initiator additives. Magnetic ferrospheres were isolated from coal combustion ash using a combination of magnetic separation, hydrodynamic, and granulometric methods. The physicochemical characteristics of the ferrospheres, including bulk density, pycnometric density, specific surface area, particle size distribution, and chemical composition, are presented in Table 1.

The choice of ferrospheres as initiator additives is explained by their high content of iron oxides, which, depending on the processing conditions, can exhibit initiator or catalytic activity. In addition to their functional properties, ferrospheres represent an accessible and low-cost raw material, and their application contributes to the utilization of industrial waste generated by thermal power plants.

Table 1: Characteristics of magnetic ferrospheres from thermal power plant (TPP) ash

Physicochemical characteristics of magnetic ferrospheres	Values of Technical Parameters
Bulk density. g/cm³	1,85
Pycnometric density, g/cm³	3,67
Specific surface area, m²/g	0,35
Diameter of ferrosphere fractions, mm	0,25 - 0,45
Ingredients, mass % SiO_2,	4,05
Al_2O_3	1,92
Fe_2O_3	85,18
CaO	8,71
MgO	1,02
SO_3	0,27
Na_2O	0,27
K_2O	0,05
TiO_2	0,20

Prior to use in thermal cracking experiments, the magnetic ferrospheres were subjected to thermal treatment in a muffle furnace. Calcination was carried out at 800 °C in an air atmosphere for 2 h in order to oxidize divalent iron compounds to their trivalent form. As a result of this treatment, magnetite (Fe_3O_4) contained in the ferrospheres was converted to hematite (α-Fe_2O_3), which led to the loss of magnetic properties and an increase in redox activity. The phase composition of the ferrospheres before and after thermal treatment was determined by X-ray diffraction analysis using Cu-Kα radiation. The diffractograms were recorded on an X'Pert Pro MRD Panalytical powder diffractometer, and the quantitative phase composition is presented in Table 2. According to the analysis, the samples also contained 10–24 % of an amorphous phase.

Table 2: Composition of crystalline phases in magnetic microspheres

Phase	Composition of Crystalline Phases in Ferrosphere Samples, Mass %	
	After Calcination	Before Calcination
Ferrospinel	15,5	68,4
Hematite	82,0	27,5
Quartz	2,6	4,9

Calcined ferrospheres were used as initiator additives and introduced into the reaction mass in an amount of 10 %, as indicated in the article. Thermal cracking was carried out in a tubular furnace. During the cracking process, the pressure was recorded using a manometer. After thermal cracking, the reactor was removed from the furnace and cooled to room temperature.

Thermal cracking experiments were carried out in a tubular reactor placed in an electrically heated furnace at temperatures ranging from 350 to 500 °C. The pressure during the cracking process was monitored using a manometer, after which the reactor was cooled to room temperature.

The gaseous products formed during thermal cracking were collected from the reactor through a needle valve. After gas collection, a sample of approximately 100 mg was taken for thermogravimetric analysis. The remaining thermolysis products were subjected to extraction and separation procedures.

The content of resins and asphaltenes in the obtained products was determined using standard methods. Asphaltenes were precipitated with n-hexane at a ratio of 40 volumes. After washing, the hexane solution was combined with the deasphalted oil, and the excess solvent was removed by evaporation. The resulting maltenes were applied to a silica gel layer at a ratio of 1:15, after which fractionation was performed. The separated resin and asphaltene fractions were subsequently analyzed using structural–group analysis methods.

All thermal cracking experiments were performed at least twice under identical conditions. The deviation between parallel experiments did not exceed ±3 %, which confirms the reproducibility of the obtained results.

Results and Discussion

The material composition of the products obtained was determined to evaluate the transformations of fuel oil components derived from heavy paraffinic crude oil during the thermolysis process. The corresponding data illustrating the effect of temperature and initiator additives on product distribution are presented in Figures 1 and 2.

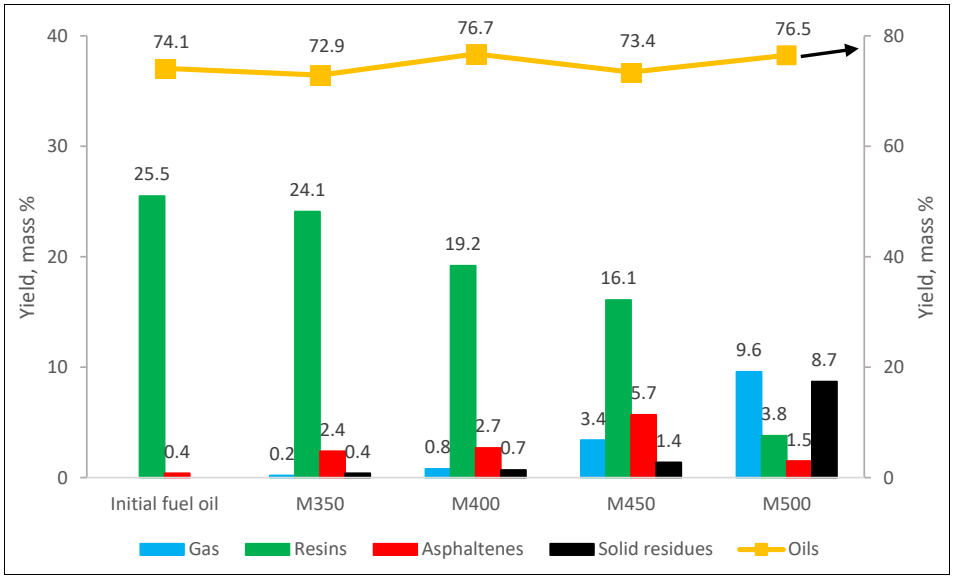

Fig 1: Material composition of thermal cracking products obtained without the use of FS

As can be seen from Figure 1, during the thermal cracking of fuel oil carried out in the temperature range of 350–500 °C without the use of FS, the content of resins decreases with increasing temperature: while it is 25.5 mass % in the initial fuel oil, this value decreases to 3.8 mass % in the products obtained at 500 °C. At the same time, the yield of solid and gas products increases; their contents vary in the ranges of 0.4–8.7 mass % and 0.2–9.6 mass %, respectively.

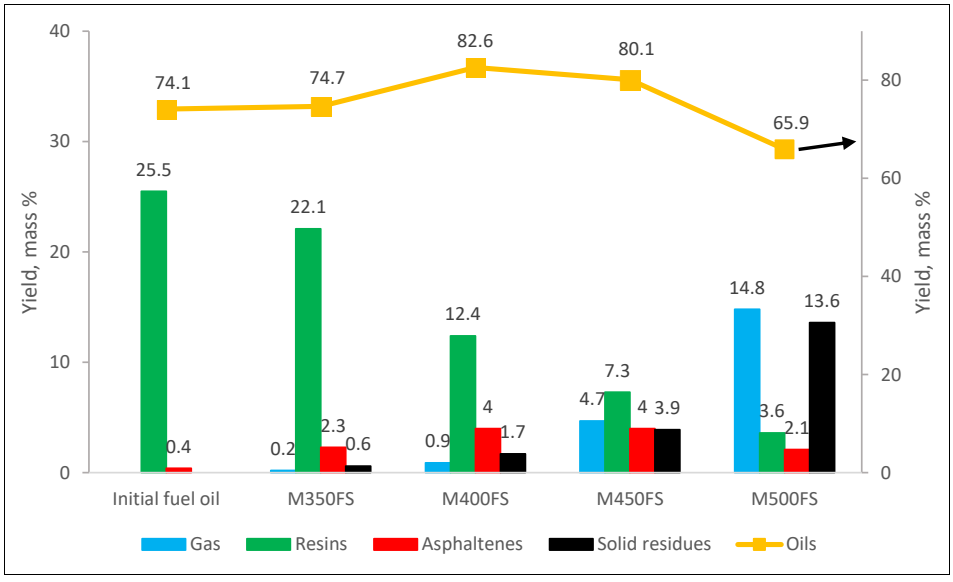

Fig 2: Material composition of thermal cracking products obtained with FS

When the process temperature is increased from 450 to 500 °C, pronounced changes in the composition of the products are observed. In this case, the proportion of solid products increases from 1.4 to 8.7 mass % (more than sixfold), while the content of asphaltenes and resins decreases by almost four times. Based on the obtained data, it can be concluded that the destruction of resins begins at 400 °C and proceeds especially intensively at temperatures above 450 °C. The destruction of asphaltenes, as well as the formation of solid and gas products, is also most pronounced at temperatures above 450 °C.

When the temperature is increased from 350 to 500 °C, the yield of oils does not change significantly and varies from 74.1 mass % in the initial fuel oil to 76.5 mass % at 500 °C.

The direction of transformations and the yield of target products can be influenced by initiator additives; therefore, the effect of FS was investigated. During the thermal cracking of fuel oil in the presence of FS, the yield of resins decreases significantly compared to the products obtained without FS (Figures 1 and 2).

A noticeable difference in the product composition is observed in the temperature range of 400–450 °C. At 400 °C, the introduction of FS reduces the yield of resins by 1.5 times, and at 450 °C by 2.2 times, compared to the products obtained at the same temperatures without initiator additives. At the same temperatures, a noticeable increase in the yield of oils is also observed. The obtained data show that in the presence of FS, at temperatures of 400–450 °C, the oil content increases by 5.9–6.7 mass %.

Further increase in temperature to 500 °C in the presence of FS leads to a decrease in the oil yield to 65.9 %, while the

shares of gas and solid products increase to 14.8 and 13.6 mass %, respectively.

Thus, it can be assumed that the addition of FS accelerates the resin destruction process (Figure 2).

The activity of FS is explained by the presence of hematite and its ability to participate in oxidation–reduction reactions, as well as by the selective sorption of resins and asphaltenes on its surface. It is reported in the literature that resins and asphaltenes are readily adsorbed on transition metal oxides, including iron oxides.

The fractional composition of thermal cracking products (fractions with a boiling temperature up to 360 °C), calculated relative to the initial feedstock, is presented in Tables 3 and 4.

Table 3: Fractional composition of thermal cracking products of petroleum residues without FS

Fraction	Initial Fuel Oil	M350	M400	M450	M500
IBP-200°C	0	0,7	1,5	6,2	52,5
200-360°C	9,8	13,7	15,5	21,8	18,6
> 360°C	64,3	58,7	60,6	45,2	5,5

Table 4: Fractional composition of thermal cracking products of petroleum residue in the presence of FS

Fraction	Initial Fuel Oil	M350FS	M400FS	M450FS	M500FS
IBP-200°C	0	0	1,0	2,5	45,6
200-360°C	9,8	15,2	20,2	24,4	14,3
> 360°C	64,3	59,5	62,3	53,3	6,3

The introduction (application) of FS does not have a significant effect on the yield of fuel fractions (fractions with a boiling temperature up to 360 °C); however, it makes it possible to reduce the total yield of resin–asphaltene components by almost two times and to increase the total yield of fractions with boiling temperatures above 360 °C. These changes in the material composition positively affect certain consumer properties of the obtained products—such as viscosity and pour point—since the presence of resin–asphaltene components and solid paraffins directly influences these parameters.

Conclusion

The results of this study indicate that the application of ferrosphere-based initiator additives significantly influences the transformation of resin–asphaltene components during the thermal cracking of heavy paraffinic fuel oil. Although the introduction of ferrospheres does not lead to a substantial increase in the yield of light fuel fractions with boiling temperatures up to 360 °C, it markedly reduces the total content of resin–asphaltene components, in some cases by nearly twofold.

The presence of ferrospheres intensifies the destruction of resins at temperatures of 400–450 °C, which is accompanied by an increase in the oil fraction yield. At higher temperatures (500 °C), the initiator promotes deeper conversion of heavy components, resulting in increased formation of gas and solid products. The observed activity of ferrospheres can be attributed to the redox properties of hematite and the selective adsorption of resins and asphaltenes on iron oxide surfaces.

Overall, ferrospheres derived from thermal power plant ash can be considered an effective and low-cost initiator additive for regulating the transformation pathways of heavy petroleum residues. Their use not only improves the composition of thermolysis products but also contributes to the utilization of industrial waste, making the proposed approach technologically and environmentally attractive for heavy oil processing.

References

1. Speight JG. The chemistry and technology of petroleum. CRC press, Boca Raton, 2014, 953.
2. Головко А. К. Крекинг тяжелого нефтяного сырья с использованием каталитических добавок на основе ферросфер энергетических зол.//Катализ в промышленности,2015:4:65-72.
3. Li J, Zhou T, Tang X, Chen X, Zhang M. Viscosity reduction process of heavy oil by catalytic co-pyrolysis with sawdust // Journal of Analytical and Applied Pyrolysis,2019:140:444-451.
4. Mousavi M, Abdollahi T, Pahlavan F, Fini EH. The influence of asphaltene-resin molecular interactions on the colloidal stability of crude oil. // Fuel,2016:183:263-271.
5. Simon İA, James Speight. Petroleum resins : separation , character, and role in petroleum: separation, in petroleum. Petroleum Science and Technology,2001:19(1-2):1-34.
6. Liu D, Li C, Yang F, Sun G, You J, CuiK. Synergetic effect of resins and asphaltenes on water / oil interfacial properties and emulsion stability. // Journal of Analytical and Applied Pyrolysis,2019:252:581-588.
7. Demirbas A, Bafail A, Nizami AS. Heavy oil upgrading: Unlocking the future fuel supply //Petroleum Science and Technology,2016:34(4):303-308.
8. Speight JG, Pancirov RJ. Structural types in petroleum asphaltenes as deduced from pyrolysis/gas chromatography/mass spectrometry //Liquid Fuels Technology,1984:2(3):287-305.
9. Абилова Г. Р. и др. Содержание и соотношение ванадия и никеля в смолах тяжелых нефтей //НефтеГазоХимия,2017:2:25-31.
10. Taherpour A. *et al*. Application of Fuzzy c-means algorithm for the estimation of Asphaltene precipitation //Petroleum Science and Technology,2018:36(3):239-243.
11. Liu D. *et al*. Synergetic effect of resins and asphaltenes on water/oil interfacial properties and emulsion stability //Fuel,2019:252:581-588.
12. Макаревич, В.Н. Ресурсный потенциал месторождений тяжелых нефтей европейской части Российской Федерации. / В.Н. Макаревич, Н.И. Искрицкая, С.А. Богословский // Нефтегазовая геология. Теория и практика,2012:7(3):13.
13. Zhang L. Degradation of recalcitrant naphthenic acids from raw and ozonated oil sands process-affected waters by a semi-passive biofiltration process. / L. Zhang, Y. Zhang, M.G. El-Din // Water Res,2018:133:310–318.
14. Капустин ВМ. Нефтеперерабатывающая промышленность США и бывшего СССР. / В.М. Капустин, С.Г. Кукес, Р.Г. Бертолусини - М.: Химия, 2015, 304.
15. Rana MS. A review of recent advances on process technologies for upgrading of heavy oils and residua. / M.S. Rana, V. Samano, J. Ancheyta, *et al*. // Fuel,2011:86:1216–1231.