THE STRUCTURAL CHANGES OF ASPHALTENES DURING HYDROCONVERSION

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Introduction

ASPHALTENES

- Are the heaviest aromatic component of crude oil
- Are precipitated on the catalyst surface and block the pore mouth
- Act as coke precursors
- May limit the maximum level of feedstock conversion

Catalyst deactivation

1. Investigation of the structure, composition and properties of macromolecular weight components
2. Study of their behavior and features of transformations during refining

→ Increase the efficiency of refining and control the process parameters and feedstock conversion

Introduction

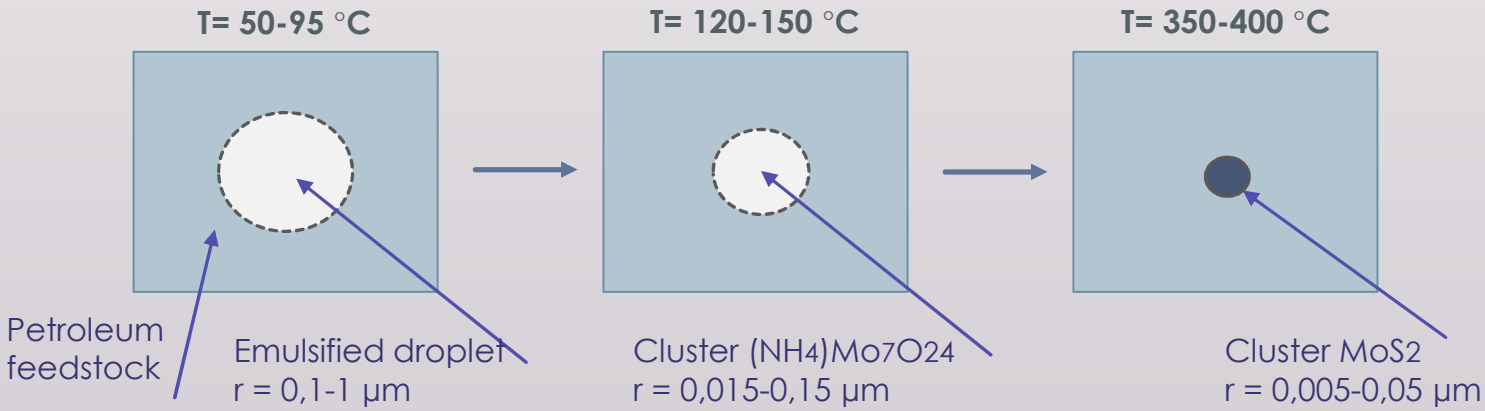
Hydroconversion in the presence of nanosized catalyst particles MoS_2

Refining of different feedstock regardless of content:
- heteroatoms;
- heavy metals;
- asphaltenes and resins.

Process provides:
- high conversion of feedstock;
- low coke formation;
- decrease in the pressure to 6-7 MPa.

Catalyst precursors – Water-soluble salts of catalytically active metals, that are introduced as emulsions followed by conversion to the slurry in heat treatment

Synthesis of nanosized catalyst particles "in situ" in the reaction zone:



Experimental part

1st experimental session:

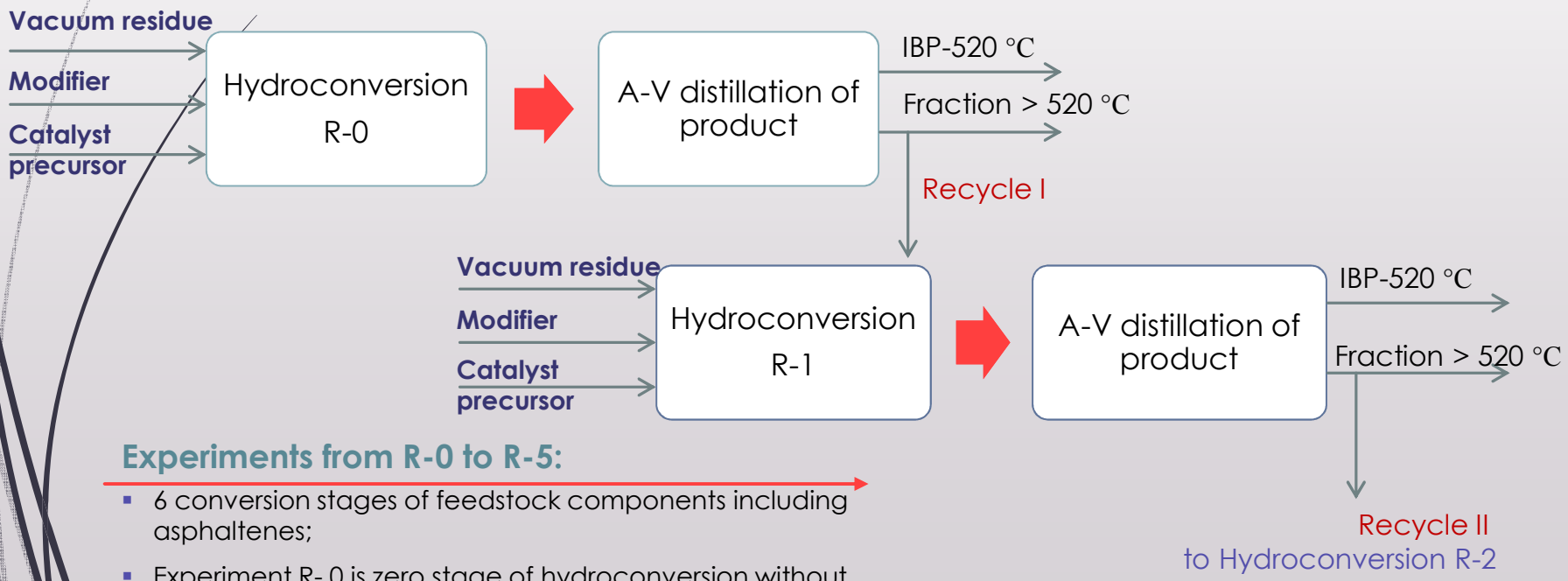
Various temperatures (425, 440, 445 и 450 °C)

- *T* = 425–450°C, *P* = 7.0 MPa, liquid hourly space-velocity (LHSV) of 2,0 - 2,2 h^{-1}, and hydrogen/feedstock ratio up to 1000 n L/L

2nd experimental session:

Various number of asphaltene conversion stages in the reaction zone

- *T* = 440–445°C, *P* = 7.0 MPa, liquid hourly space-velocity (LHSV) of 1.5 h^{-1}, and hydrogen/feedstock ratio up to 1000 n L/L



Experiments from R-0 to R-5:

- 6 conversion stages of feedstock components including asphaltenes;
- Experiment R- 0 is zero stage of hydroconversion without recycle.

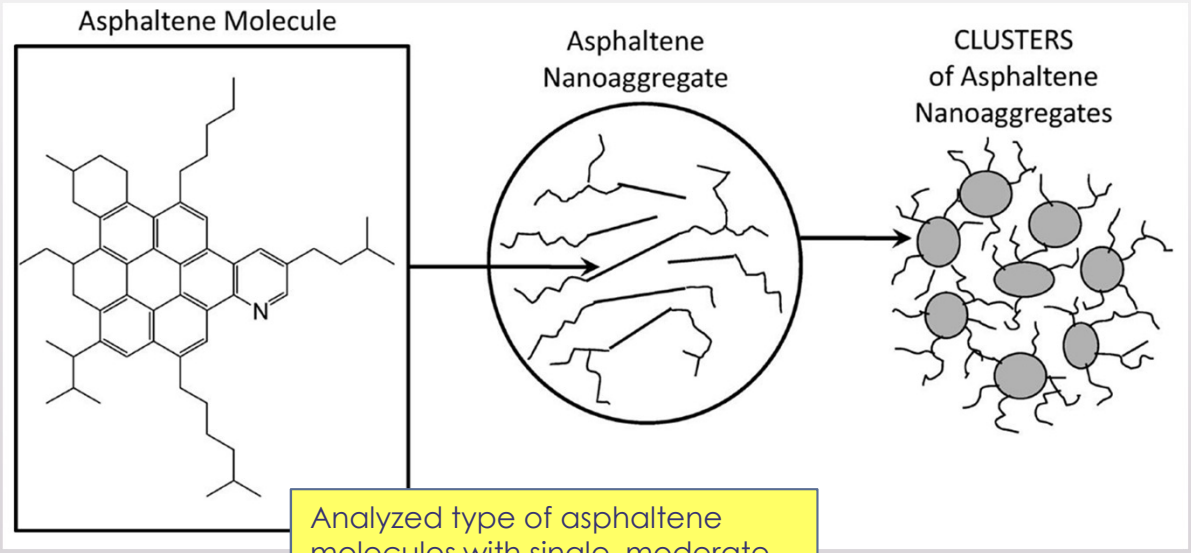
Object of investigation

Asphaltenes from petroleum feedstock

Asphaltenes from hydroconversion products

Molecular structure

Colloidal structure



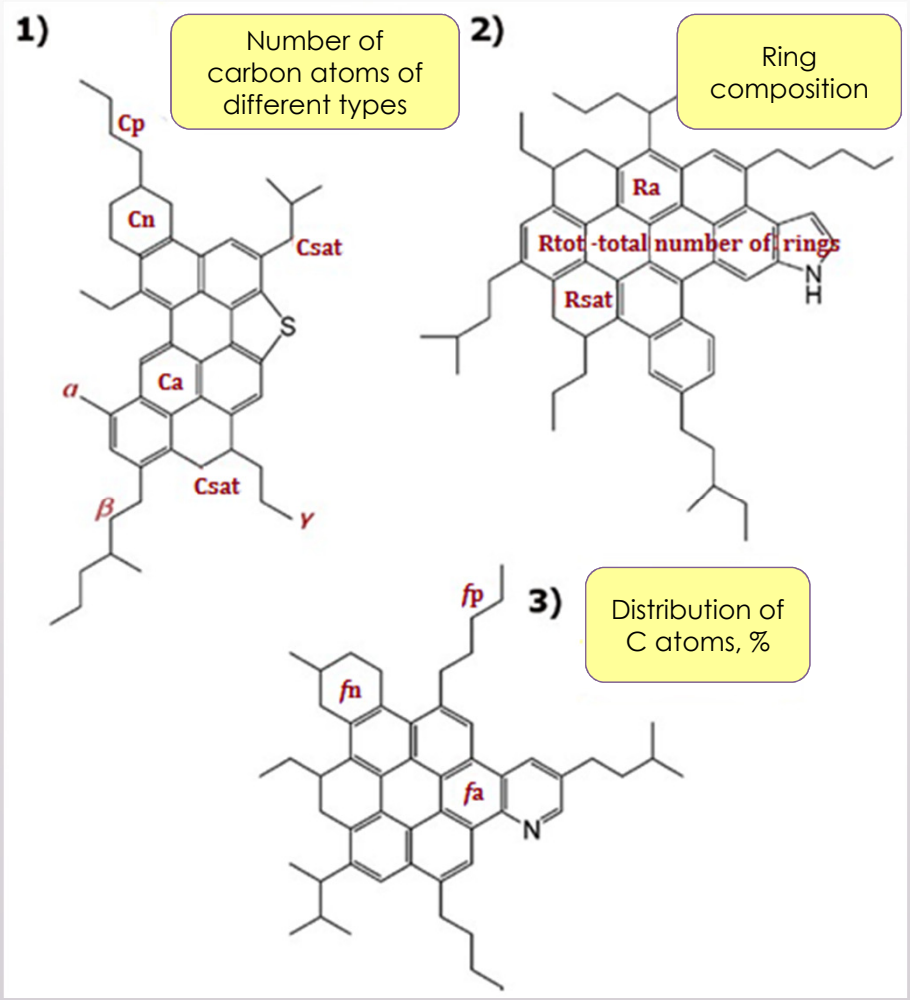
Analyzed type of asphaltene molecules with single, moderate-sized polycyclic aromatic hydrocarbon (PAH) ring system with peripheral alkanes

The structural parameters of asphaltene molecules

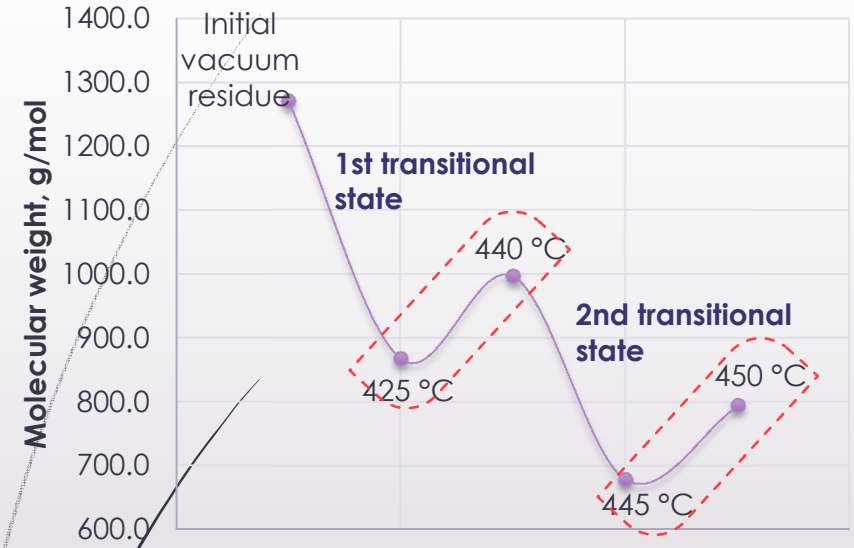
- Elemental composition;
- Average molecular weights;
- Distribution of hydrogen atoms;

Structural group analysis

Average distribution of carbon atoms between the structural elements



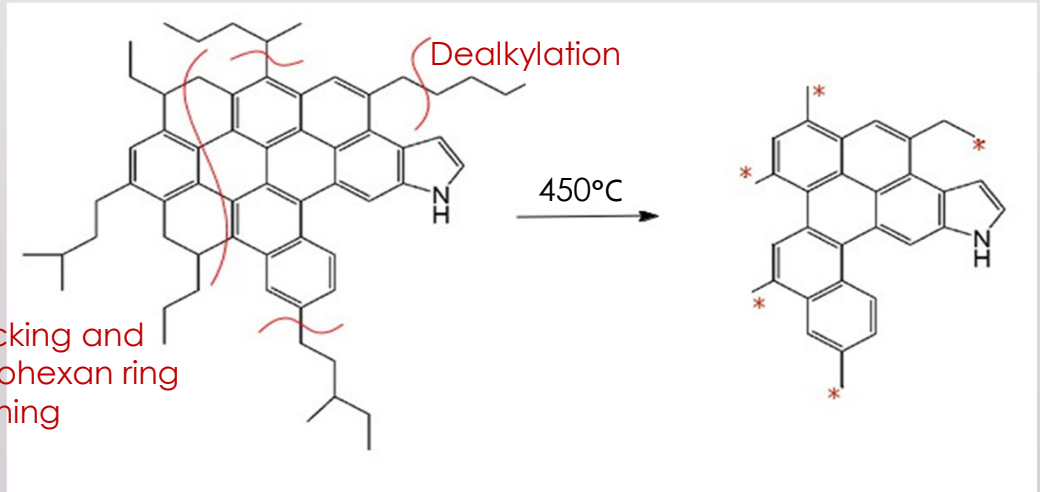
Change in molecular weight of asphaltenes at various temperatures



One of the main features is the ***nonmonotonic character*** of changes in MW.

It has been noted:

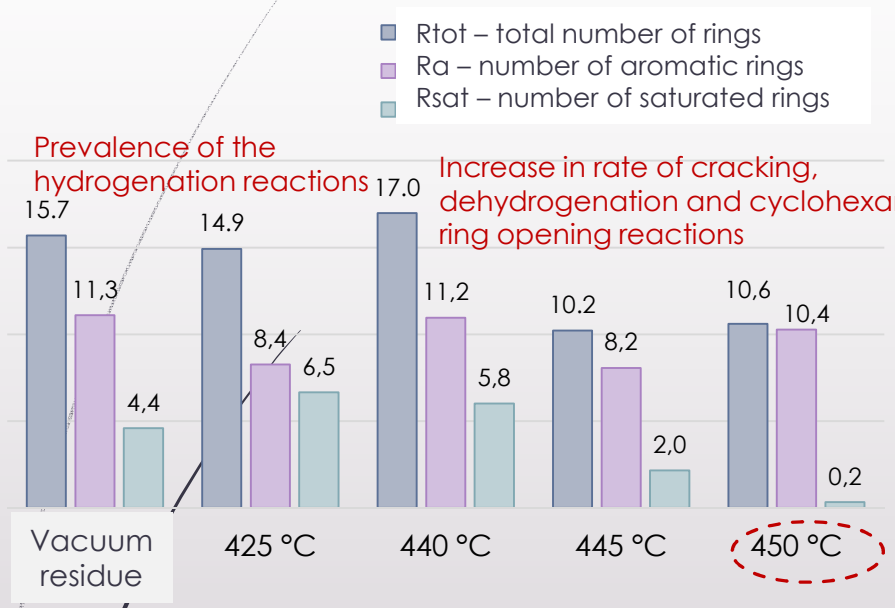
- ***Characteristic temperature ranges*** – 425-440 °C and 445-450 °C;
- Low temperatures (below 425 °C) and the range 440-445 ^{0}C – ***transitional states***.



Nucleation and growth in the asphaltene structure of a mesophase

Change in the ring composition (1), the amount of aromatic and saturated carbon atoms (2) in the structure of asphaltene molecules

1



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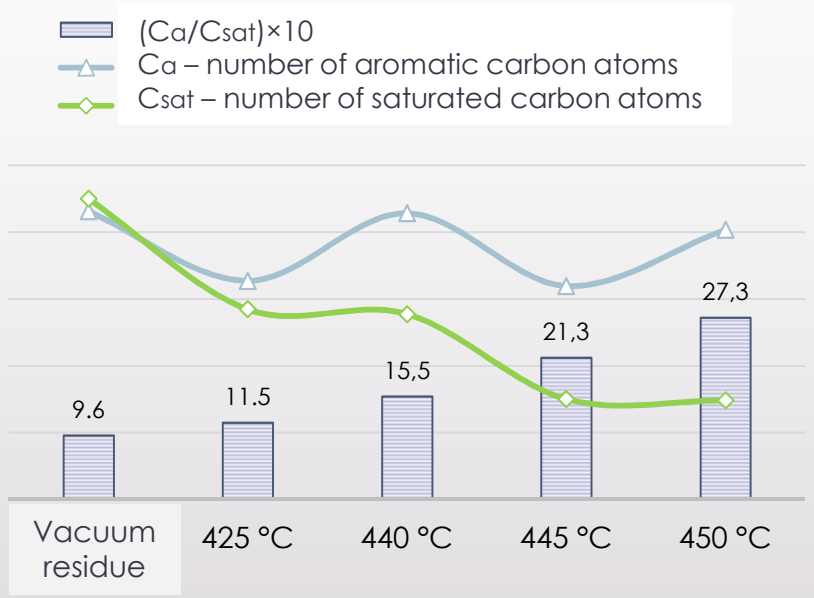


Increase in the hydroconversion temperature

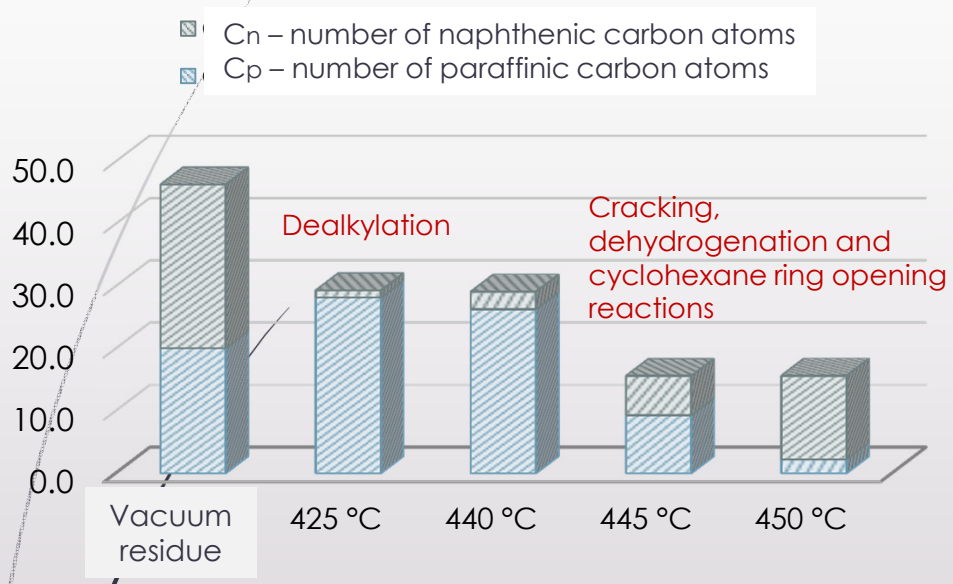
Stability of the size of the condensed aromatic core (Ra≈const)

Increase in the proportion of unsubstituted aromatic rings (Ra/Rtot ≈1)

- Redistribution of carbon between aromatic and saturated fragments (Ca/Csat>1);
- Increase in aromaticity;
- Stability of the size of the condensed aromatic core (Ca≈ const)

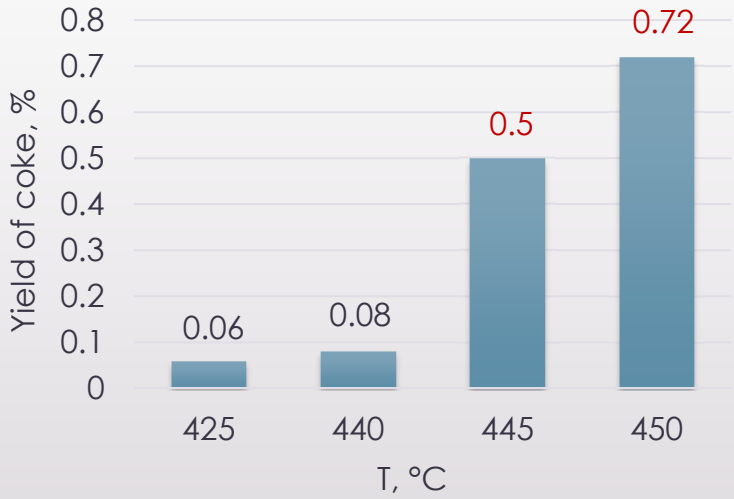
Change in the amount of carbon atoms in naphthenic and paraffinic (1), influence of temperature on the yield of coke (2)

1



*column height corresponds to the total number of Csat

2



Increase in the hydroconversion temperature to 440^0 C → Increase in the amount of unsubstituted aromatic rings → Nucleation and growth in the asphaltene phase of a mesophase → Significant increase in the amount of coke

Scheme of structural transformations of asphaltene molecules depending on hydroconversion temperature

Reduction in the amount saturated structures in the condensed naphthenic-aromatic core by considerable enhancement cracking and cyclohexan ring opening reactions; insignificant change in the amount of Ra

2nd TRANSITIONAL STATE

Asphaltenes of hydroconversion products (425-440°C)

Prevalence of saturated over aromatic structures Ca/Csat < 1

a) Increase in aromaticity by the rise in the rate of dehydrogenation reactions of Rsat
b) Low extent of suppression of hydrogenation reactions, stability of Rtot in the condensed naphthenic-aromatic core
c) High degree of dealkylation

a) Increase in the rate of dehydrogenation reactions, decrease in the degree of dealkylation
b) Stability of Rtot
c) Increase in the proportion of unsubstituted aromatic fragments

Asphaltenes of vacuum residue

Asphaltenes of hydroconversion products (445-450°C)

1st TRANSITIONAL STATE

• Prevalence of the hydrogenation reactions of aromatic fragments;
• High rate of dealkylation Ca/Csat > 1

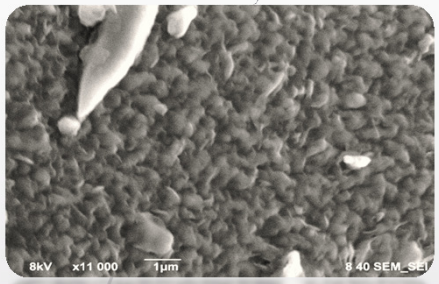
INCREASE IN THE HYDROCONVERSION TEMPERATURE

- Reduction in MW by the cracking, dealkylation and C-S, -N, -O bond opening reactions;
- Stability of the condensed aromatic core;
- Redistribution of carbon between aromatic and saturated fragments (Ca/Csat>1); increase in the aromaticity.

Change in asphaltene morphology depending on hydroconversion temperature

SEM images

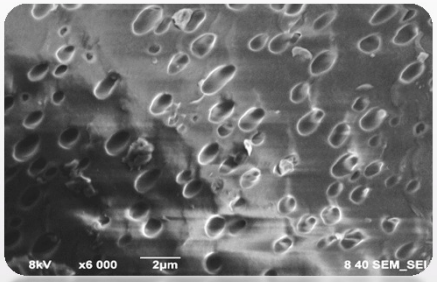
Asphaltenes from initial vacuum residue



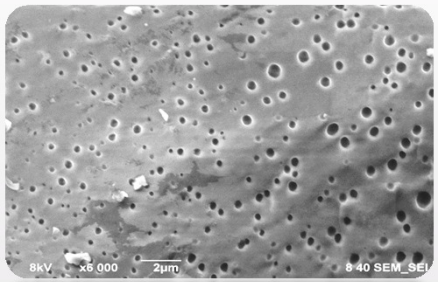
▪Rough structure formed by the asphaltene aggregates, which are adsorbed on the surface of the resins.

1st transitional state

Asphaltenes from hydroconversion products at various temperatures



425°C



440°C

▪Smooth surface with pores;

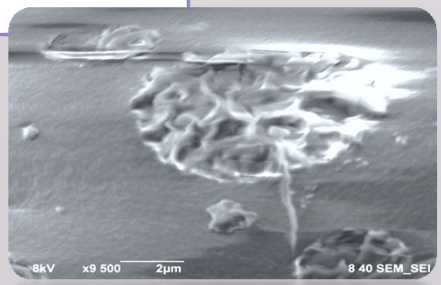
▪Increasing temperature reduces pore size

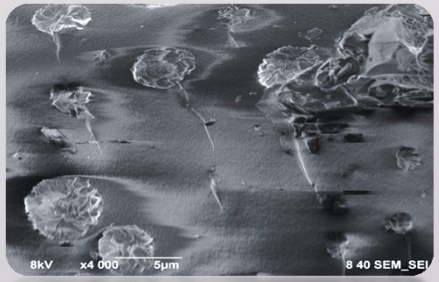
2nd transitional state

Removal of alkyl chains and increase in the proportion of unsubstituted aromatic fragments

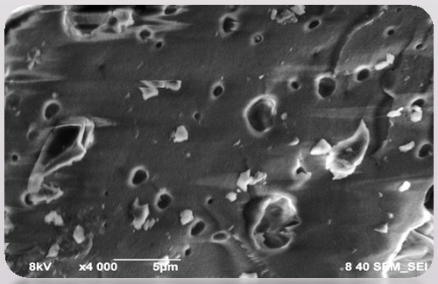
▪Formation of stereospecific condensed structure in two-dimensional *plane;*

▪ Nucleation and growth in the asphaltene phase of a ***mesophase***





450°C



445°C

Change in asphaltene morphology depending on hydroconversion temperature

SEM images

The complex structural unit of resin-asphaltene constituents

The core (dispersed particles) is formed by paramagnetic asphaltene molecules

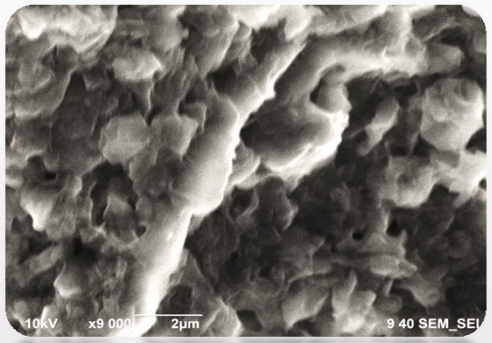
Adsorption-solvate layer composed of diamagnetic resin molecules and mono-, bi-, polycyclic aromatics

Spatial redistribution of macromolecular components and colloidal asphaltene structures

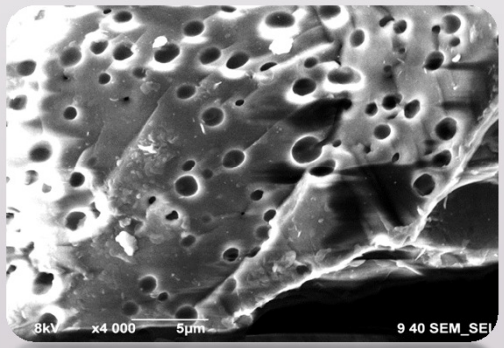
Aqueous solution of catalyst precursor

Structured interfacial layer (asphaltenes and resins)

Emulsion – vacuum residue/ aqueous solution of catalyst precursor

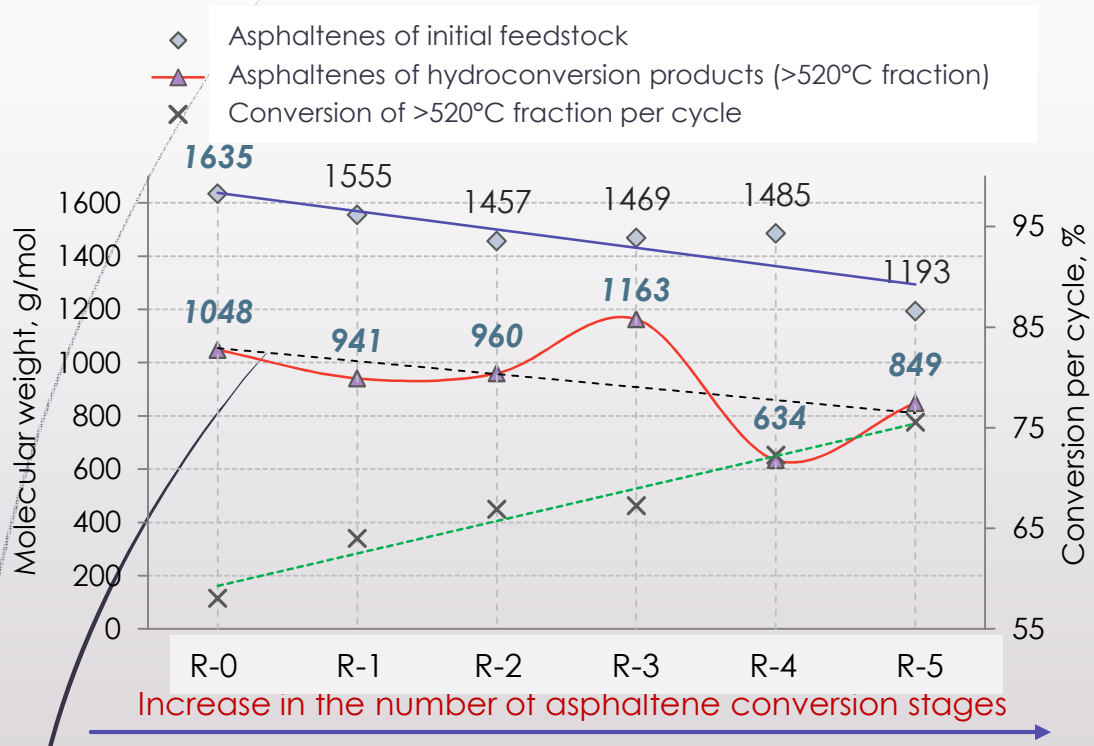


Slurry – vacuum residue/ nanosized catalyst particles MoS_2



Synthesis of catalytically active phase MoS_2 "in situ" in the reaction zone → Additional dispergation of colloidal asphaltene structures, resins desorption → Increase in efficiency of contact between reactive molecules, catalyst and hydrogen

Change in molecular weight depending on the number of asphaltene conversion stages



Increase in the feedstock conversion per cycle

Decrease in MW of asphaltenes from processing products compared to MW of 1635 g/mol for initial feedstock asphaltenes

Nonmonotonic character of changes in MW

Asphaltenes from vacuum residue

1st transitional state

Zero stage of hydroconversion (R-0)

Asphaltenes from hydroconversion products

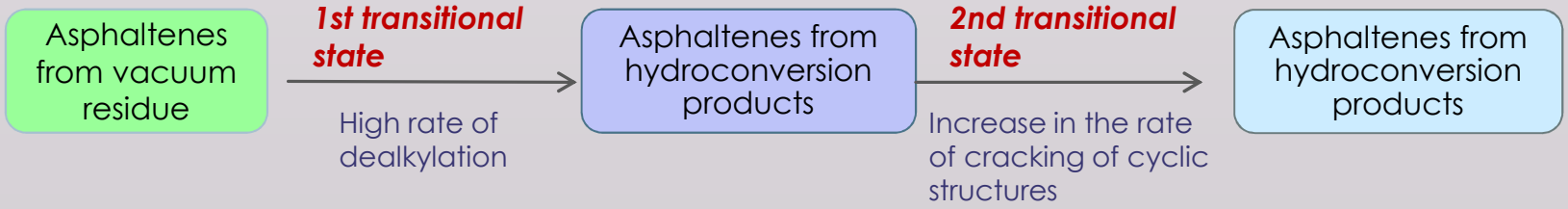
2nd transitional state

On the boundary between R-3 and R-4

Asphaltenes from hydroconversion products

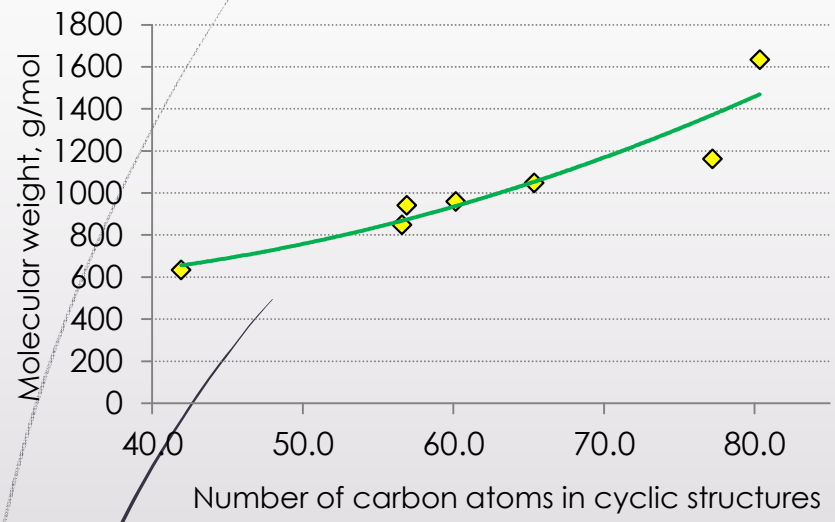
Average structural parameters for asphaltene molecules

Parameter	Asphaltenes of initial feedstock	Asphaltenes of hydroconversion product at different numbers of conversion stages					
		R-0	R-1	R-2	R-3	R-4	R-5
Average number of atoms in molecule							
C	110.2	73.2	65.1	67.7	82.7	43.6	58.7
H	118.2	61.7	58.0	56.4	70.0	38.5	50.3
N	2.0	1.7	1.4	1.6	2.0	0.8	1.2
S	3.7	1.8	1.8	1.7	2.2	0.8	1.2
O	2.9	1.5	1.5	0.8	0.1	2.2	2.4
Ring composition							
Ra	16.3	13.8	11.6	13.1	15.3	7.3	10.2
Rsat	4.6	2.8	2.9	2.2	4.3	3.2	4.0
Rtot	20.9	16.6	14.5	15.3	19.6	10.5	14.2
Average number of carbon atoms of different types in molecule							
Ca	61.4	53.4	45.0	50.9	59.2	28.7	39.6
Csat	48.8	19.8	20.1	16.8	23.5	14.9	19.1
Cc	80.3	65.4	56.9	60.2	77.2	41.9	56.6
Cn	18.9	12.0	11.9	9.3	18.0	13.2	17.0
Cp	29.9	7.8	8.2	7.5	5.5	1.7	2.1



Correlation of MW with the proportion of C atoms in the cyclic structures (1), change in the amount of heteroatoms depending on the amount of aromatic C atoms (2)

1)



Stability of the condensed aromatic core (Ra≈const)

Variation of temperature

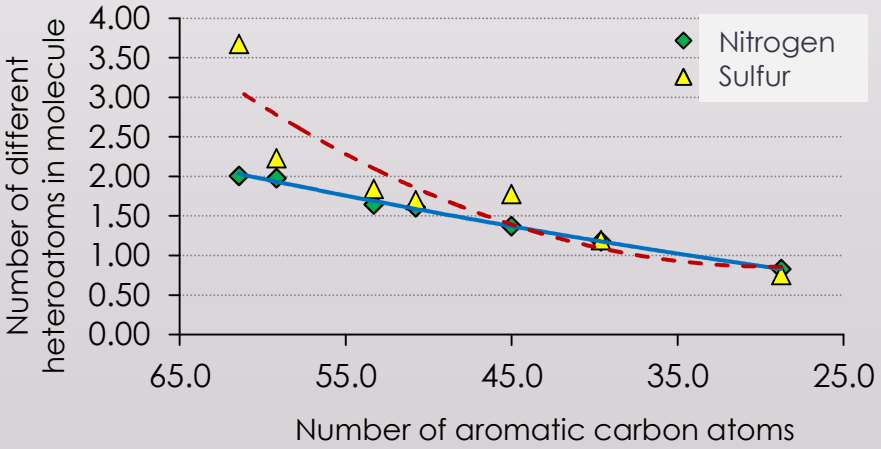
Change in the number of recycling stages

Destruction of cyclic fragments including the most stable heteroaromatic structures having low reactivity, with the high reaction rate of dealkylation

As the number of asphaltene conversion stages increases, the amount of the most reactive compounds of sulfur decreases

Level of denitrogenation is less than desulfurization

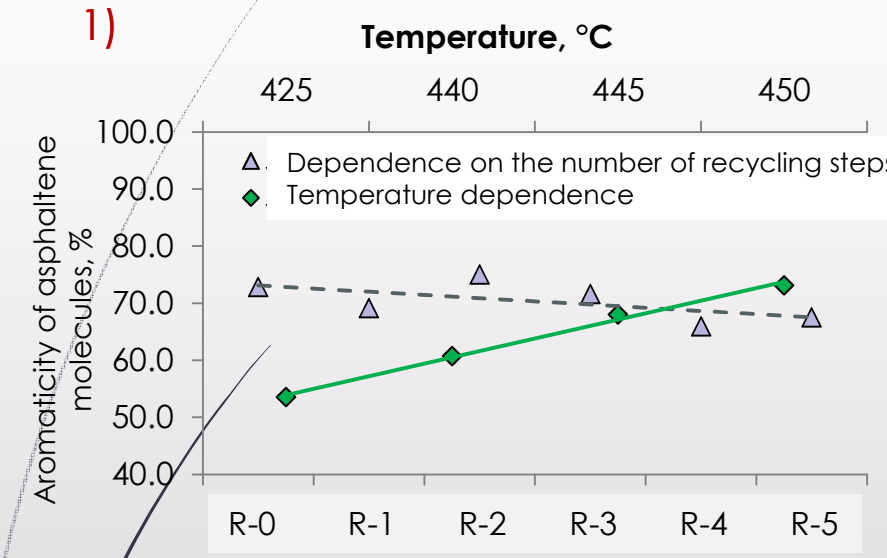
2)



Increase in the number of asphaltene conversion stages

Dependence of the aromaticity (1) and the yield of condensation products (2) on the temperature and the number of conversion stages

1)



Even and continuous growth of aromaticity molecules

Increase in the hydroconversion temperature

Increase in the number of recycling stages

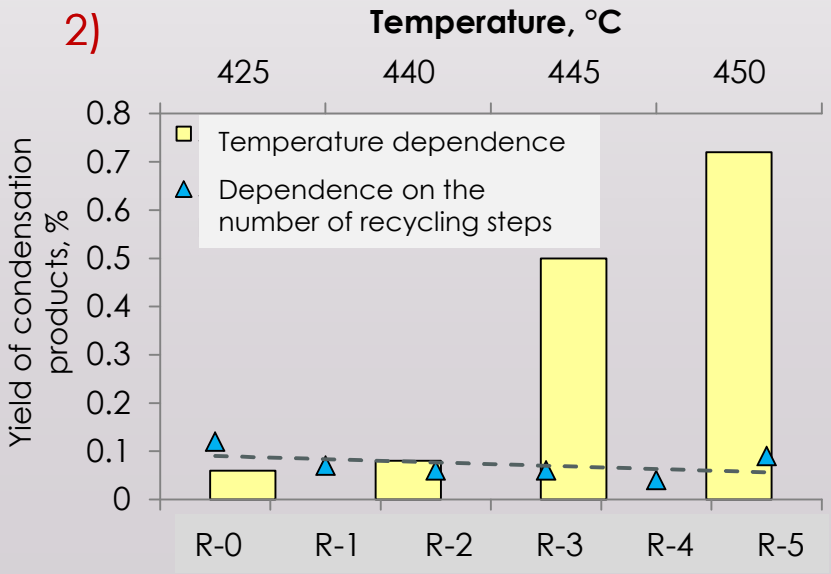
Decrease in aromaticity molecules

Increase in the hydroconversion temperature to 440^0 C

Increase in the amount of unsubstituted aromatic rings

Significant increase in the amount of coke

2)



Conclusion

- It is shown that, the molecular structure of asphaltenes depending on different process conditions vary in a discrete manner, passing through a step of *transitional state* (*TS*), in which system is the most susceptible to the action of external factor.
- It is noted that, the changes in the structural parameters of asphaltene molecules at each TS step are due to the prevalence of characteristic reactions, which are similar as in variation of temperature and change in the number of recycling stages. However, there are significant differences between structural transformations of asphaltenes depending on various process parameters.
- Investigations of changes in asphaltene morphology confirm the main features of the structural transformations of asphaltenes, which were established by structural-group analysis of asphaltene molecules. It is shown that the quality rearrangement of the asphaltene molecular structure by passing through the TS, where the system is most active, leads to quality changes in the asphaltene morphology and change of colloidal-chemical structure of the system.
- Hydroconversion parameter intervals, corresponding to the TS, are the most favorable in terms of regulation of structural transformations of macromolecular components and increasing level of conversion with low coke formation.

Thank you for attention!