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CATALYTIC HYDROPROCESSING IN OIL REFINING

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Developing of multiscale approach to HPC-simulation of multiphase fluid flows

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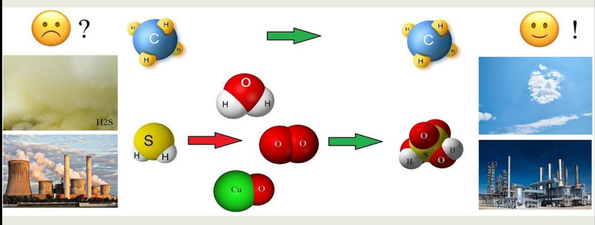
MAIN PROBLEM

Purification of natural gas (NG) from various kinds of contaminants (metal particles, solid organic compounds, etc.)

- constructing the scheme of an industrial installation for cleaning natural gas from sulfur impurities
- developing the multiscale multicomponent mathematical model of natural gas and different kinds impurities flow analysis



INSTALLATION FOR CLEANING: CYCLES

At each of the three stages of the presented cycle of the installation, some gaseous or liquid substance is passed through the system. Accordingly, three mathematical descriptions of this process are formed.

I. NG cleaning:

NG is passed through installation. At the start, the scrubber is filled with atmospheric air under standard conditions. Inert gases are represented only by argon. With the NG entering the scrubber, there are only methane and hydrogen sulfide in variable mass fractions. NG is supplied at increased pressure, but at the same temperature. NG accumulates in porous material and is transformed into pure methane and hydrogen sulfide oxidation products (for ex., H_2SO_4) when interacting with MeO chemisorbents (for ex., ZnO, CuO, etc.). Catalytic reaction in chosen case is written in the following form:

$$H_2S + MeO \dashrightarrow MeS + H_2O.$$

As a result, purified methane and water vapor are obtained at the outlet of the scrubber. The porous material retains water and sulphide MeS, which will be removed at the second stage of processing.

II. Flushing the scrubber with water:

a stream of hot water with a temperature of *340-360 K* with a large proportion of atmospheric air dissolved in it is passed through the scrubber. Getting into the pores, the water reduces the MeO oxides and flushes out the sulfuric acid. The final catalytic reaction in this case is written as follows:

$$H_2O + 2O_2 + MeS \dashrightarrow MeO + H_2SO_4.$$

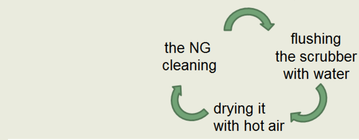
III. Drying it with hot air:

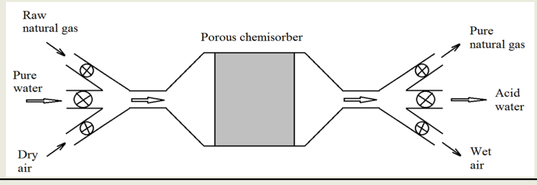
hot air stream is passed through the scrubber to remove the water remaining in pores.

INSTALLATION FOR CLEANING NATURAL GAS

The installation structure is the simplest scrubber, in which the central part is filled with a porous material, which purifies NG by the adsorption-catalytic method.

A feature of the installation is the alternation of cycles:





MULTISCALE MULTIPHASE MATHEMATICAL MODEL FOR FLOW OF LIQUID OR GAS MIXTURE WITH IMPURITIES

The model consists of four parts:

1) The first part is related to the macroscopic scale of the treatment system and includes quasigasdynamic (QGD) equations [1-3], describing the flow of gaseous fluids.
2) The second part used the quasihydrodynamic (QHD) equations [1-3], describing the liquid fluids.
3) The third part include reaction-convection-diffusion (RCD) equations for impurity concentrations.
4) The fourth part of the model describes processes in boundary layers and is based on the equations of analytical chemistry (ACh) [4] and molecular dynamics (MD) [5].

The aim of the work was a physically justified implementation of the conjugation of parts of the model.

Quasigasdynamic (QGD) equation system for gas mixture:

$$\frac{\partial \rho_i}{\partial t} + \operatorname{div} \mathbf{W}_i^{(\rho)} = 0, \quad \mathbf{W}_i^{(\rho)} = \rho_i (\mathbf{u}_i - \mathbf{w}_i), \quad \mathbf{w}_i = \tau \left[(\mathbf{u}_i, \nabla) \mathbf{u}_i + \frac{1}{\rho_i} \nabla p_i \right];$$

$$\frac{\partial}{\partial t} \rho_i u_{i,k} + \operatorname{div} \mathbf{W}_i^{(\rho u_k)} = S_i^{(\rho u_k)}, \quad S_i^{(\rho u_k)} = \nu_{ii} \rho_i (\bar{u}_{i,k} - u_{i,k}) \quad (k = 1,2,3),$$

$$\mathbf{W}_i^{(\rho u_k)} = \rho_i \mathbf{u}_i u_{i,k} + \mathbf{e}_k \left(p_i + \frac{2}{3} \mu_i \operatorname{div} \mathbf{u}_i \right) - \mu_i \left(\nabla u_{i,k} + (\nabla, \mathbf{e}_k) \mathbf{u}_i \right) - \rho_i \left(w_{i,k} \mathbf{u}_i + \mathbf{w}_i u_{i,k} \right);$$

$$\frac{\partial}{\partial t} E_i + \operatorname{div} \mathbf{W}_i^{(E)} = S_i^{(E)}, \quad S_i^{(E)} = \nu_{ii} \rho_i (\bar{E}_i - E_i),$$

$$\mathbf{W}_i^{(E)} = \rho_i (\mathbf{u}_i - \mathbf{w}_i) H_i - \chi_i \nabla T_i + \left(\frac{2}{3} \mu \operatorname{div} \mathbf{u}_i \right) \mathbf{u}_i - \sum_{k=1,2,3} \mu \left(\nabla u_{i,k} + (\nabla, \mathbf{e}_k) \mathbf{u}_i \right) + (\rho_i \mathbf{w}_i, \mathbf{u}_i) \mathbf{u}_i;$$

$$E_i = \frac{1}{2} \rho_i |\mathbf{u}_i|^2 + \rho_i \varepsilon_i, \quad p_i = Z_i \rho_i \Re_i T_i, \quad \varepsilon_i = c_{V,i} T_i.$$

Quasihydrodynamic (QHD) equation system for liquid flow:

$$\operatorname{div}(\mathbf{u} - \mathbf{w}) = 0, \quad \mathbf{w} = \frac{\tau}{\rho} \left[\rho (\mathbf{u} \cdot \nabla) \mathbf{u} + \nabla p \right],$$

$$\frac{\partial \mathbf{u}}{\partial t} + \operatorname{div}((\mathbf{u} - \mathbf{w}) \otimes \mathbf{u}) + \frac{1}{\rho} \nabla p = \frac{1}{\rho} \operatorname{div} \Pi, \quad \Pi = \Pi_{NS} + \rho \mathbf{u} \otimes \mathbf{w}, \quad \Pi_{NS} = \nu \rho \left[(\nabla \otimes \mathbf{u}) + (\nabla \otimes \mathbf{u})^T \right],$$

$$\frac{1}{\rho} \Delta p = -\operatorname{div} \left[(\mathbf{u} \cdot \nabla) \mathbf{u} \right] + \frac{1}{\tau} \operatorname{div} \mathbf{u}.$$

Reaction-Convection-Diffusion equations for NG fractions:

$$\frac{\partial C_k}{\partial t} + \operatorname{div} \mathbf{W}_k^{(C)} = F_k, \quad \mathbf{W}_k^{(C)} = -D \nabla C_k + \mu_k^{(C)} \mathbf{u} C_k, \quad k = 1, \ldots, m;$$

C_k - concentrations of reagents $\qquad F_k = G_k - R_k$ - reaction terms

Molecular dynamics:

$$\begin{cases} m_l \dfrac{d\mathbf{v}_{l,i}}{dt} = \mathbf{F}_{l,i}, & \mathbf{F}_{l,i} = -\dfrac{\partial U(\mathbf{r}_{i,1}, \ldots, \mathbf{r}_{i,N})}{\partial \mathbf{r}_{l,i}} + \mathbf{F}_{l,i}^{ext}, \\ \dfrac{d\mathbf{r}_{l,i}}{dt} = \mathbf{v}_{l,i}, & i = 1, \ldots, N_l, \quad l = 1, \ldots, N_{tot} \left(N_{tot} \equiv N_{gas} + N_{mat} \right), \end{cases}$$

$\mathbf{r}_{l,i} = (r_{x,l,i}, r_{y,l,i}, r_{z,l,i})$ - radius vector of particle

$\mathbf{v}_{l,i} = (v_{x,l,i}, v_{y,l,i}, v_{z,l,i})$ - velocity of particle

$\mathbf{F}_{l,i} = (F_{x,l,i}, F_{y,l,i}, F_{z,l,i})$ - total force acting on a particle

GENERAL COMPUTATIONAL ALGORITHM

1) At the initial stage of calculations, the microgeometry of the porous chemisorber and an unstructured adaptive grid are generated that describes the computational domain.

2) The initial equilibrium distribution of the gas-air mixture in the installation is set, corresponding to standard conditions. And then the calculation of the first operating mode of the installation is made, in which the NG flows into the scrubber, fills the chemisorber and begins to be purified. The process is modeled until noticeable degree of purification of NG leaving the scrubber is registered.

3) The initial data for the second stage calculation are the results of previous calculations. The supply of NG to the installation is stopped and the supply of sufficiently hot water with a high content of atmospheric air is turned on. The calculation is carried out until the sulfuric acid content in the fluid reaches a predetermined minimum value.

4) After obtaining the results of calculations for flushing the installation, you can use the data obtained to calculate the drying process of the installation with a stream of hot atmospheric air. The calculation process is completed when the required degree of oxidant reduction in the pores of the chemisorber is reached.

NUMERICAL AND PARALLEL TECHNIQUES

1) On macro-level the numerical procedure use the splitting into physical processes, unstructured meshes, finite volume method, expicit finite-difference schemes on time.

2) On micro-level we use the combination of PiC method and molecuar dynamics approach based on the Verlet scheme.

3) Parallelization of algorithms on macro-level based on domain decomposition technique and rational distribution of grid sub-domains on the nodes of supercomputer.

4) Parallelization of algorithms on micro-level use the domain decomposition technique and load balancing between CPU or GPU cores into supercomputer node.

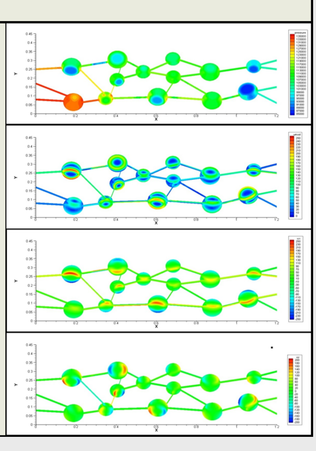
5) The elaborated parallel software use the MPI, OpenMP and CUDA technologies.

CALCULATIONS

Passage of gaseous fluid (methane-hydrogen sulfide mixture in a ratio of 75:25) through chemisorber was performed in a 2D setting. At the initial moment, a moderate pressure drop was set at the inlets and outlets of the segment (*dp = 32500 Pa*). The flow was considered isothermal at a temperature of *293.15 K*. The calculation was carried out before the flow parameters reached steady state.

The results of calculating the flow parameters are shown in Figure. They are distributions (from top to bottom) of pressure, modulus, and longitudinal and transverse velocity components during the passage of methane-hydrogen sulfide mixture through the pore space of the chemisorber.

They show the main paths of the fluid flow, where stagnant zones and plugs are formed. As for the results of fluid purification, sulfide is formed in all areas of the surface of the pore structure, but over time it moves into its stagnant zones. On the one hand, this fact contributes to the cleaning process. However, it will also interfere with the regeneration of the chemisorbent.



CONCLUSIONS

1) A new multiscale mathematical model of natural gas purification processes from harmful impurities, primarily sulfur impurities and its derivatives is proposed.
2) The model is based on a combination of macro- and microscopic descriptions of the processes of transfer of fluid components and their interaction with a catalyst on the pore surface.
3) The general numerical algorithm is based on splitting by physical processes and combines grid methods and methods of analytical chemistry and molecular dynamics.
4) The work presents an example of a numerical calculation of the flow of natural gas in a fragment of the pore space of a chemisorber, which confirms the efficiency of the proposed approach.

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