The chemical energy unit partial oxidation reactor operation simulation modeling

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Abstract. The chemical energy unit scheme for synthesis gas, electric and heat energy production which is possible to be used both for the chemical industry on-site facilities and under field conditions is represented in the paper. The partial oxidation reactor gasification process mathematical model is described and reaction products composition and temperature determining algorithm flow diagram is shown. The developed software product verification showed good convergence of the experimental values and calculations according to the other programmes: the temperature determining relative discrepancy amounted from 4 to 5 %, while the absolute composition discrepancy ranged from 1 to 3%. The synthesis gas composition was found out practically not to depend on the supplied into the partial oxidation reactor (POR) water vapour enthalpy and compressor air pressure increase ratio. Moreover, air consumption coefficient \(\alpha\) increase from 0.7 to 0.9 was found out to decrease synthesis gas target components (carbon and hydrogen oxides) specific yield by nearly 2 times and synthesis gas target components required ratio was revealed to be seen in the water vapour specific consumption area (from 5 to 6 kg/kg of fuel).

1. Introduction

The energy resources and petrochemical feedstock providing is the indispensable prerequisite of every country economy successful development. The natural organic raw materials main sources are oil, natural gas, coal, oil shale and biomass. Nowadays, the most demanded chemical and energy resources are oil and natural gas [1]. Their production is reaching the highest level possible and in the near future is to reduce. Consequently, the importance of the organic raw materials alternative sources such as oil sludge, gas condensate, etc., increases. To overcome the petroleum feedstock shortage, the synthesis gas (syngas) large-scale production according to the energy and technology principle with the pyrolysis and gasification technologies application has started [2-4]. Practically all the most important petrochemical products are assumed to be obtained by the synthesis gas chemical processing.

2. The problem statement

Taking into account the foregoing, the consideration of energy and technology units for energy carriers (heat and electric power) and synthesis gas combined generation by gas condensate gasification seems to be quite relevant. The chemical energy units with fuel partial oxidation (gasification) establishment near hydrocarbon deposits and synthesis gas major consumers will make possible not only to provide them with energy carriers, but also with the process gas for various industries. The unit heat diagram is shown in figure 1. In case of economic expediency, the chemical
energy unit operation including the third party consumers supply with carbon dioxide and gaseous nitrogen is possible to be organized.

The unit operates in the following way. The partial oxidation reactor 3 consumes air, process oxygen (98% O₂) or their mixture (oxygen enriched air) from the compressor 1 and/or air separation unit 2 and water (blow) vapour from the vapour waste heat boiler 6 for liquid or gaseous fuel gasification process performing. The generated reaction products enter the gas turbine 4, which drives the electric generator 5.

![Diagram](image)

Figure 1. The basic heat diagram of the chemical energy unit including process gas, electric and heat energy producing: 1 – compressor; 2 – air separation unit; 3 – partial oxidation reactor; 4 – gas turbine; 5 – electric generator; 6 – vapour waste heat boiler; 7 – contact condenser; 8 – water treatment system; 9 – condensate water pump; 10 – condensate water cooler; 11 – condensate water filter; 12 – water storage tank; 13 – condensate pump; 14 – deaerator; 15 – feed pump; 16 – separator; 17 – scrubber for the acid gas absorbing by the liquid absorber; 18 – regenerative heat exchanger; 19 – liquid absorber regenerator; 20 – refrigerator; 21 – liquid absorber heater for regeneration.

The exhaust synthesis gas with the pressure required for processing equipment aerodynamic resistance overcoming and synthesis processes normal conducting is fed to the waste heat boiler 6 where it is cooled and then directed to the contact condenser 7 where water vapour which enters the water storage tank 12 condenses. Then synthesis gas is supplied into the scrubber for the acid gas absorbing by the liquid absorber 17 for the further treatment and equivalence ratio bringing to the required values according to the synthesis gas further use technology regulations. The synthesis gas prepared in this way, consisting of nitrogen, hydrogen and carbon monoxide, is transferred to the technological consumer or can be used to generate energy carriers (heat and electric energy). Treated as above synthesis gas consisting of nitrogen, hydrogen and carbon oxide is supplied to the process consumer or
is possible to be used for energy carriers (heat and electric power) generation. The part of the vapour produced in the waste heat boiler 6 is supplied into the partial oxidation reactor 3, while the remained vapour is sold to the consumers. Gas turbine unit electric generator 5 generates electric power transferred to the end-users. From the water storage tank 12 through the condensate water cooler 10, where condensate water is cooled by the process water from the recycling water supply system and condensate water filter 11 by applying the condensate water pump 9 and water treatment system 8 connected with the process water supply line to the water treatment system, cooled water is supplied to the contact condenser 7. The condensate from the consumer is returned into the water storage tank 12, where from through the deaerator 14 by using the condensate pump 13 and feed pump 15, the feed water passes through the waste heat boiler 6 economizer and evaporative section and enters the separator 16 where it is decomposed into vapour and water. Water vapour passes through the waste heat boiler 6 superheater zone and enters the partial oxidation reactor 3 as well as it is supplied to the consumer, while water returns to the deaerator 14. The absorber saturated with acid gas from the scrubber for acid gas absorbing by the liquid absorber 17 is supplied to the regenerative heat exchanger 18 where it receives heat from the regenerated absorber and to the liquid absorber regenerator 19 where the regeneration occurs. It should be noted that the part of the regenerable absorber is bled from the liquid absorber regenerator bottom 19 and passes through the liquid absorber heater for regeneration 21 where it is heated by the heating neat-carrier from the regenerative absorber heating system until it returns to the regenerator. The regenerated absorber is fed to the heat exchanger 18 where the heat is transferred to the absorber saturated with acid gas, then to the refrigerator 20 where it is cooled by the process water from the liquid absorber cooling system before returns to the scrubber for acid gas absorbing by the liquid absorber 17.

The most interesting from the simulation modeling point of view is the partial oxidation reactor (POR) represented in figure 2 which can be considered as the plug-flow reactor. Fuel, air and/or oxygen as well as water vapour are supplied to this unit for H₂ content in the synthesis gas bringing to the required by the consumer values. Oxidizing agent is fed less than the stoichiometric value. The POR operating process is similar to gas turbine combustion chambers one, however, it has its own peculiarities and is defined by the specific conditions of aerodynamics, chemically-reacting system, heat exchange, temperature level, structural and geometric dimensions.

![Figure 2](image)

**Figure 2.** The chemical energy unit partial oxidation reactor sketch: Gₐ – air and water vapour mixture entering the POR chamber; Gₓ – reaction products entering the gas turbine; F – fuel entering the atomizer; D – POR chamber diameter; L – POR chamber length.

Burning due to lack of oxidizer and reaction products composition calculation as well as the theoretical reaction temperature determination are more difficult compared to the complete oxidation since gases should contain such components as CO and H₂ along with the complete combustion products when equilibrium state is reached.

3. Theory
To evaluate the reaction products quantitative and qualitative characteristics and POR mass-dimensional parameters, it is necessary to develop the mathematical model. The gas-generating process calculation algorithm basic flow diagram is presented in figure 3.
When developing the mathematical model, the following assumptions not impacting the research results accuracy were admitted: the reaction products are evenly (perfectly) mixed and in the equilibrium state, in this case at any point of the reaction mixture the reaction products composition will be the pressure and temperature function. The assumption is characteristic of the other authors works, for example [4, 5, 6].

The reaction products equilibrium composition defining reduced to solving the nonlinear algebraic equations system including the material balance equations in chemical elements constituting the initial fuel, the equilibrium constant equation for which the defining reaction is CO conversion reaction by water vapour (water gas reaction [5]) as well as Dalton equation defining the total pressure connection with the synthesis gas individual components partial pressures. The obtained synthesis gas composition was calculated by the following main components: carbon oxide, carbon dioxide, methane, hydrogen, water vapour and nitrogen.
Figure 3. Gas-generating process calculation algorithm flow diagram.
Taking into account the presented methodological postulates and materials [7], the reaction products composition, their temperature and flow calculating program [8] considering the initial fuel process composition impact, fuel flows and blowing vapour ratios, oxidizing agent as well as POR pressure and temperature was developed in C++ environment and registered.

The programme operating principle is based on the iterative calculations by using the least squares method and relies on theoretical temperature determining followed by its comparison and necessary basic data preliminary determination in the corresponding programme blocks.

The program makes possible to take into account CO₂ and H₂O dissociation (more than 1773 K and 1873 K correspondingly [9]) at the high temperatures. Carbon dioxide α₀ and water vapour β₀ dissociation degrees depending on their partial pressures and temperature T_p are identified according to the reference data presented in [9] before heat losses from the carbon dioxide and water vapour dissociation are determined, kJ/kg:

\[
q_D = 12640 \cdot \alpha_D \cdot v_{CO_2} + 10800 \cdot \beta_D \cdot v_{H_2O}
\]  

(1)

Reaction products theoretical temperature is determined taking into account the formula (1) by the expression, K:

\[
T_j = \frac{Q^0}{v_{N_2} \cdot c_{N_2} + v_{CO_2} \cdot c_{CO_2} + v_{H_2O} \cdot c_{H_2O} + v_{CO} \cdot c_{CO} + v_{H_2} \cdot c_{H_2} + v_{SO_2} \cdot c_{SO_2}} + 273
\]

(2)

where \(Q^0\) is the gas condensate combustion specific heat, kJ/kg; \(\alpha\) is the oxidizer flow coefficient (air); \(L_0\) is the dry air specific consumption for the fuel unit complete combustion, m³/kg; \(t_{air}\) is the oxidizer temperature (air), °C; \(c_{cond}\) is the fuel heat capacity (gas condensate), kJ/(kg·K); \(t_{cond}\) is the fuel temperature (gas condensate), °C; \(G\) is the specific consumption of vapour supplied to POR, kg/kg of gas condensate; \(h\) is the enthalpy of vapour supplied to POR, kJ/kg; 10800 is the hydrogen low heating value, kJ/m³ [9]; 12640 is the carbon oxide low heating value, kJ/m³ [9]; \(v\) is the synthesis gas individual components theoretical yield, m³/kg; \(c\) is the synthesis gas individual components heat capacity, kJ/(kg·K).

4. Experimental results

To verify the proposed mathematical model, the calculations by using [8] and the Aspen HYSYS oil and gas processing manufacturing procedures accurate modeling system representing the software package for the chemical and engineering productions modeling, designing, optimization and business planning in the field of hydrocarbons production and processing and petrochemicals were performed. In this case the software product Aspen HYSYS performs the plug-flow, perfect-mixing, equilibrium, stoichiometric reactors calculation. The results obtained by using mathematical models and experimental data are presented in tables 1 and 2.

Table 1 shows the results of methane conversion to air blowing at the air consumption coefficient of \(\alpha = 0.34\), the initial methane-air mixture heating to 400 °C and the pressure of 101.325 kPa; table 2 presents the experience and calculations results of the initial methane-air mixture heating combining to 315 °C and air enrichment to 26% of oxygen at \(\alpha = 0.42\) and the pressure of 101.325 kPa.

| Parameter, UM | Value |
|---------------|-------|
| **Synthesis gas composition, volume %** |       |
| N₂            | 46.5  |
|               | 46.2  |
|               | 45.9  |
| H₂O           | 5.7   |
|               | 7.2   |
|               | 4.9   |
| CO₂           | 2.6   |
|               | 0.7   |
|               | 1.4   |
Table 2. POR calculation results comparison with the factual data.

| Parameter, UM | Value |
|---------------|-------|
|               | Experimental data [11] | The calculation by applying [8] | The calculation by applying the software product Aspen HYSYS |
| Synthesis gas composition, volume | | | |
| N<sub>2</sub> | 43.0 | 49.2 | 49.6 |
| H<sub>2</sub>O | 9.9 | 16.0 | 15.3 |
| CO<sub>2</sub> | 3.8 | 3.0 | 2.7 |
| CO | 14.8 | 13.7 | 14.1 |
| H<sub>2</sub> | 26.0 | 18.1 | 18.3 |
| CH<sub>4</sub> | 1.4 | 0.0 | 0.0 |
| C<sub>2</sub>H<sub>n</sub> | 1.1 | 0.0 | 0.0 |
| Synthesis gas temperature, °C | 1187 | 1569 | 1440 |

The results presented in tables 1 and 2 demonstrate the obtained POR research tool adequacy as a software product which calculation results showed good convergence of the experimental values and calculations according to the other programmes: the temperature determining relative discrepancy amounted from 5 to 25 %, while the absolute composition discrepancy ranged from 3 to 6%. Such a high synthesis gas temperature discrepancy is likely explained by not taking into consideration the heat losses into the environment in the mathematical models which in fact constitutes a high value and ranges from 250 to 380 °C.

The composition and parameters calculation results of the produced gas from the condensate of the following composition: CH<sub>4</sub>=16.1%; C<sub>2</sub>H<sub>6</sub>=3.1%; C<sub>3</sub>H<sub>8</sub>=1.6%; i-C<sub>4</sub>H<sub>10</sub>=1.1%; n-C<sub>4</sub>H<sub>10</sub>=1.0%; i-C<sub>5</sub>H<sub>12</sub>=0.5%; n-C<sub>5</sub>H<sub>12</sub>=0.9%; C<sub>6</sub>=73.8%; CO<sub>2</sub>=1.8%; CH<sub>3</sub>OH=0.1% at h=2681 kJ/kg; t<sub>condensate</sub>=–27 °C are represented in figures 4 and 5.

Moreover, during the preliminary calculations performing [7] the synthesis gas composition was found out practically not to depend on the supplied to POR water vapour enthalpy and compressor pressure increase ratio.

Figure 4. The synthesis gas components specific yield

Figure 5. The synthesis gas composition dependence on...
dependence on the air consumption coefficient at $\pi_c=5$ and $G=0$ kg/kg: 1 is nitrogen; 2 is water vapour; 3 is carbon dioxide; 4 is carbon oxide; 5 is hydrogen.

Figure 4 analysis shows that the air consumption coefficient $\alpha$ increase from 0.7 to 0.9 reduces the synthesis gas target components specific yield (carbon oxide and hydrogen) by almost 2 times, while as $\alpha$ reaches the stoichiometric value (value 1.0), the reaction products become the combustion products. Figure 5 shows that the synthesis gas target components required ratio is observed in the field of the water vapour specific consumption from 5 to 6 kg/kg, however, there will be the increased value of the unreacted water vapour content in the synthesis gas from 45 to 49 % that will impose certain peculiarities on the gas turbine, vapour waste heat boiler, and contact condenser operation.

The reactor geometry calculation results depending on the pressure created by the chemical energy unit compressor at the gas condensate oxidation of 1400 kg/h with the specific combustion heat of $Q_l=44847$ kJ/kg for the various POR chamber heat stresses corresponding to the forced (lines 4 and 5) and unforced (lines 1, 2 and 3) operation are represented in figure 6.

Figure 6. POR diameter dependence on pressure: 1 is 24 W/(m$^2$·Pa); 2 is 72 W/(m$^2$·Pa); 3 is 120 W/(m$^2$·Pa); 4 is 360 W/(m$^2$·Pa); 5 is 600 W/(m$^2$·Pa).

As can be seen in figure 6 the transfer from the atmospheric pressure to the increased one ($\pi_c=5$) makes it possible to reduce the POR diameter by almost 2.2 times from 3050 mm to 1350 for the unforced operation (line 1, figure 6) and by 2.4 times for the forced one (line 5, figure 6). Thus, it can be concluded that under the same POR pressure range, the most preferred operation mode is the forced one reducing the unit specific amount of metal (capital investments). Furthermore, figure 6 shows that the considerable pressure influence on POR diameter practically ceases in the range of $\pi_c=30-36$ for the unforced operation mode (line 1, figure 6) and $\pi_c=10-15$ for the forced one (line 5, figure 6).

5. Results and discussion

Thus, according to the results of the carried out preliminary studies, the POR calculating programme which is possible to be integrated into the complete chemical energy unit complex mathematical description was developed. On the basis of this programme the synthesis gas composition was found out practically not to depend on the enthalpy of the supplied to POR water vapour and the compressor air pressure ratio, and consequently these parameters can be optimized on the assumption of the system thermodynamic analysis and economic efficiency defining principles. Based on the trend to the synthesis gas target components content maximum, it is necessary to approach the air consumption coefficient minimum value by the soot formation condition, i.e. to $\alpha = 0.7$ for which the water vapour specific consumption appropriate value at the range from 5 to 6 kg/kg of gas condensate was chosen. Furthermore, relying on the works performed at the given stage it is quite obvious that the POR forced
operation mode will provide its geometric dimensions minimization, besides the dimensions need to be specified by using the chemical kinetics, heat and mass transfer and aerodynamics methods.

6. Conclusions
It can be concluded that the developed fuel partial oxidation products composition calculation procedure as part of the chemical energy units is applicable at the stage of the main and auxiliary equipment implementation and operating parameters optimization variants preliminary scientific investigations and feasibility elaborations.

The air consumption coefficient increase α from 0.7 to 0.9 was found out to reduce the synthesis gas target components specific yield by 2 times from 1 m³/kg of gas condensate on CO and from 0.5 m³/kg of gas condensate on H₂ by means of calculation. For the considered gas condensate composition, the synthesis gas target components required ratio is observed in the water vapour specific consumption range from 5 to 6 kg/kg of gas condensate that can be explained by the low hydrogen content of the initial fuel.

The POR diameter variants calculations results showed that it is possible to recommend the most preferred operation mode, namely, the forced one decreasing the unit specific amount of metal, in this case the considerable pressure influence on POR diameter practically ceases in the range of ρ = 10-15 in the above mentioned mode.

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