Conversion of liquid combustible wastes in the filtration regime to syngas by partial oxidation

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Abstract: A new method of combustion/conversion of liquid combustible wastes is proposed in the filtration mode when one of the reagents (liquid fuel or oxidizer gas) is supplied from the end of the reactor filled with a porous incombustible backfill (inert) and the other into the middle part. In this case, the inert, charged to the upper part of the reactor at room temperature, is heated in countercurrent combustion products. At discharging of inert from the lower part of the reactor (and the equal volume is simultaneously added to the upper part, so that the bed in the reactor is kept constant), the inert heated in the upper part enters the lower part, where it gives heat to the gaseous reagent supplied from below. This method can be carried out both with an excess of the oxidant with the combustion of combustible liquids to CO2 and H2O, and with a lack of oxidizer, when the conversion of the initial fuel to the synthesis of a gas predominantly containing CO and H2 takes place. On the example of a model fuel (isopropyl alcohol), the regularities of filtration combustion at different oxidant to fuel ratios have been experimentally studied.

1. Introduction

In the world a large number of various types of liquid combustible wastes are concentrated, among which: spent organic solvents and various combustible-lubricating materials. When they are stored for a long time or improperly destroyed, very dangerous substances form from an ecological point of view.

For effective processing of such liquid combustible wastes, the process of filtration burning in a countercurrent mode can be used. By filtration combustion we mean the process of oxidation of fuel during filtration through it or a layer of inert material of a gaseous oxidant [1-5]. In the case of filtration combustion, the phenomenon of "superadiabatic heating", due to the concentration of released heat in the combustion zone due to internal heat exchange between the gas and condensed phases, can be observed [6]. The accumulation of heat in a relatively narrow combustion zone can be so great that the temperature in the front of the combustion wave can repeatedly exceed the adiabatic combustion temperature of the mixture calculated on the assumption that the initial temperature of the reagents is equal to the ambient temperature and the thermal oxidation effect of the fuel is distributed throughout the reactor volume [7–10]. The heat concentration is due to the fact that in the case of counter flow of reagents, the inert components of the system are a very effective coolant, thanks to which both the fuel and the oxidant can be heated to the maximum efficiency before reaching the zone of chemical reactions. In the regime of filtration combustion with countercurrent of reagents, such an important characteristic as the burning rate due to the high
temperature is determined not by the speed of chemical reactions, but only by the flow of reagents into the combustion zone (filtration rate) and stoichiometry of the process. This method can be carried out both with an excess of the oxidant with the combustion of combustible liquids to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \), and with a lack of oxidizer, when the conversion of the initial fuel to the synthesis of a gas predominantly containing \( \text{CO} \) and \( \text{H}_2 \) takes place [11-14]. One of the reagents (liquid fuel or oxidizing gas) is supplied from the end of the reactor filled with a porous non-flammable charge, and the other into its middle part [15-18]. In this case, the inert material charged to the top of the reactor at room temperature is heated in countercurrent combustion products. The inert material discharged from the reactor (and at the same time the equal volume is pumped into the upper part, so that the bed in the reactor is kept constant), heated in the upper part gives heat to the gaseous reagent supplied from below [19-23]. Thus, the inert is discharged from the reactor in the cool condition, and the gaseous reactant is supplied to the reaction zone at a high temperature. Such a heat exchange scheme can be used in a reactor with a moving layer of a solid inert, which will allow to operate in a continuous mode.

2. Experimental setup
The laboratory studies were performed on a vertical shaft kiln reactor (4) made of quartz with an inner diameter of 66 mm and a length of 500 mm (fig. 1). The bulk of the reactor was filled with a granular inert solid, 5× 10 mm porcelain Raschig rings. As a model hydrocarbon fuel, isopropyl alcohol (chemically pure) was used in the experiments, which is a clear, colorless, flammable liquid with a characteristic odor with a gross formula \( \text{C}_3\text{H}_8\text{O} \).

![Figure 1. Schematic of the experimental reactor.](image)

Gaseous oxidant (air) was supplied to reactor via inlet of the bin’s (7) cover. The air flow rate was controlled with an electronic “Mass-view MV-306” flow meter (9), with accuracy 2%. The product gas was carried outside from the upper end of reactor. The supply of liquid fuel to the reactor was carried out through the side inlet in the reactor (located opposite the third thermocouple) using a peristaltic pump Tholen Pumpen (5). The methodical error of fuel consumption did not exceed ± 2.5%. The isopropyl alcohol consumption in the experiments was fixed and was ~ 7 ml/min. Specific air flow varied from 0.4 to 1 l/s and was selected so that the equivalence ratio of oxidant to fuel varied from 0.4 to 1.6.

Prior to an experiment the reactor was filled with inert solid to the level of the thermocouple TC3. Further the combustion was ignited by charging into reactor 300 ml of a mixture of Raschig rings with 10% 5-mm pieces of activated coal preheated to 800 °C in a muffle furnace. Atop the ignition mixture the reactor was filled to the top with the room-temperature Raschig rings. After that, the oxidant (air) was supplied to the reactor. After burning out of the ignition mixture, the supply of liquid fuel began. Then, combustion of liquid
fuel already took place, while the high-temperature zone of combustion propagated along an inert charge in the direction of the gas flow. During the experiment, the cooled inert material was discharged by a rotating grate (8) from the reactor and the fresh portions of the inert material were loaded into the reactor. In this regime, liquid fuel was supplied to a high-temperature zone heated to above 900° C. Discharging-charging of the inert material was carried out to stabilize the high-temperature zone in one position inside the reactor (opposite the fuel supply). The discharged inert material was accumulated in storage bin (7), which made it possible to carry out long-term experiments in a quasi-continuous mode. The temperature in the reactor was measured using three Type K (chromel–alumel) thermocouples. The first thermocouple TC1 was mounted 80 mm up from the reactor bottom. Thermocouples were located on six tiers along the length of the reactor at a distance of 65 mm from each other. The readings of the thermocouples through ADC (2) were transferred to a PC (1) in real time, which made it possible to monitor the position of the combustion zone along the reactor by discharging the inert material. In the experiments periodically the product gas was sampled to a glass flask from the upper part of the reactor. The composition of the gaseous products was analyzed using a GC-CRYSTAL 5000 chromatograph, which provided a possibility to measure the concentration of substances that are gases at normal conditions. The concentration of C2-C5 hydrocarbons can be detected with an accuracy of 0.01% vol.

3. Results and discussion
Typical temperature plots for an experiment of isopropyl alcohol combustion in case of equivalence ratio of oxidant to fuel 1.6 are presented in Fig. 2. On the graph, the numbers correspond to those of thermocouples along the length of the reactor from bottom upwards. The beginning of the experiment (Ign) corresponds to the charging of the ignition mixing into the reactor and its burning. Then, the solid fuel of the ignition mixing was burned from the 3rd to the 5th minute of the experiment (tsc). After the ignition mixing was completely burned out (this moment corresponds to the shaded area in Fig. 2 and the temperature was lowered at 3-4 level of the thermocouples), liquid fuel was supplied. The stop of the fuel supply is denoted by vertical dashed line. Temperature fluctuations in this time range refer to discharging of the inert material and charging of new portions from above the reactor in order to keep the high-temperature zone opposite the fuel injection. In this experiment, liquid fuel was burned (tlc) for ~ 25 minutes. The maximum combustion temperature in the experiment was ~ 1150 ± 50° C.

![Figure 2. Typical temperature plots for an experiment of isopropyl alcohol combustion. Equivalence ratio of oxidant to fuel was 1.6. The numbers at curves correspond to those of thermocouples (from bottom upwards).](image)

The duration of the experiments was limited by the temperature at the bottom of the reactor. To avoid overheating of the rotating grate and its drive, when the temperature on the lower thermocouple (in fig. 2 – curve 1) exceeded 150 °C, the fuel supply stopped and the reactor cooled down.
Figure 3 shows the composition of gaseous products, depending on the equivalence ratio of oxidant to fuel, where 1 corresponds to the complete oxidation of the fuel to CO₂ and H₂O. As can be seen from the graphs, as the value of equivalence ratio of oxidant to fuel is increased from 0.4 to 1, the CO concentration are decrease and the increase of CO₂ (Figure 3a), as well as the decrease in the concentration of H₂ and hydrocarbons, there is no oxygen in the gaseous products (Figure 3b). With a further increase the equivalence ratio of oxidant to fuel, oxygen appears in the products, but in spite of the excess of the oxidant, the concentration of CO₂ is reduced and also CO (7-8 vol.%) is present.

Figure 3. Concentration (vol.%) of gaseous compounds of the product gas depending on the equivalence ratio of oxidant to fuel: (a) – CO₂, CO, O₂; b – hydrogen and hydrocarbons.

Also, an increase of the equivalence ratio of oxidant to fuel leads to an increase in temperature from ~ 900 ± 50 °C to ~ 1150 ± 50 °C (Figure 4) of combustion due to a decrease in specific heat loss at high oxidizer flow rates.

Figure 4. The dependences of the combustion temperature on the equivalence ratio of oxidant to fuel.

Also for comparison, thermodynamic calculations of the composition of gaseous products were carried out using the "Terra" program. The equilibrium composition of the gaseous products was calculated for a temperature range of 900-1200 °C for the C₃H₈O / air system, with a equivalence ratio of oxidant to fuel varying. In the calculations it was assumed that the air has a composition, mol. %: 21 – O₂, 79 – N₂.
In Figure 5 shows the results of the thermodynamic calculation at atmospheric pressure and temperatures 900-1200 °C.

**Figure 5.** Thermodynamic calculation of the composition of gaseous products depending on the equivalence ratio of oxidant to fuel.

Thermodynamic calculations of the composition of gaseous products are in qualitative agreement with the experimental results (see Fig. 3a). Higher values of CO and CO2 concentration are due to the fact that the calculations did not show the presence of hydrocarbons in the composition of gaseous products, whereas in the experiment they were present.

4. Conclusions

In the work, a method for burning / converting liquid organic fuels in the filtration combustion mode in a reactor with a moving layer of an inert coolant was developed and tested. Combustion of liquid hydrocarbons in the filtration mode is a promising way of utilizing various types of hazardous liquid hydrocarbon waste (waste oil, paint and varnish waste, refinery waste, and others). The advantage of burning liquid fuels (or wastes) in the filtration combustion mode is the absence of the need for the use of catalysts, which are usually used in the reforming of liquid hydrocarbon fuels.

On the example of a model fuel (isopropyl alcohol), the regularities of filtration combustion at different oxidant to fuel ratios have been experimentally studied. In the absence of an oxidizer with respect to fuel, the combustion regime is realized with the formation of a combustible gas (a mixture of carbon monoxide, hydrogen and lower hydrocarbons) with a calorific value of up to 9 MJ / m³, which can be used to produce thermal and electric energy, and also as raw materials for the chemical industry.

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