Research the content of waste (yellow oil) of the shurtan gas chemical complex in Uzbekistan

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Abstract. This article discusses the properties and composition of used oil for the purpose of processing waste oil which is a waste of the gas chemical complex to obtain secondary products and reduce its environmental damage through the efficient use of waste accumulated over the years. The study uses traditional methods for separating yellow waste oil by settling, determining the properties of the separated substances, separating dissolved gases when heating liquids, sampling and determining the gas content using a gas chromatograph and modern methods for calculating the properties of a gas mixture. As a result of the study, the physical properties of the waste oil and the oily part extracted from it were determined, the waste oil and the gases dissolved in the oil part were separated, their hydrocarbon content was determined, the properties of the gas mixture were studied. Based on the results of the study, an effective method for separating waste yellow oil was developed. The necessary information was obtained in the process of designing equipment and devices for processing the oily part. In addition to cleaning the waster oil from toxic substances released into the environment by direct degassing after installation at a temperature of 70°C, additional gaseous fuel for process furnaces can be obtained. Besides, the decomposition of emulsions can be achieved by improving the solubility in water of mineral salts mixed with oil and polymer components in the waste yellow oil. This, in turn, leads to the conclusion that degassing can accelerate the decomposition of waste oil by settling it.

1. Introduction

According to the data, today about 900 types of waste are registered. Every year, the amount of waste in the world increases by 3%. Protecting the environment from production and consumption waste is inextricably linked to the problems of rational use of these natural resources and the introduction of environmentally friendly technologies.

For many centuries, improper waste management has led to changes in natural resources and disruption of natural phenomena. At present 80 percent of the world's waste is organic matter and their processing can lead to the formation of large amounts of fuel and energy. The experience of developed countries shows that 85% of them can be recycled.

Nowadays our country pursues a consistent environmental policy aimed at protecting the environment, protecting public health, the rational use of natural resources and ensuring environmental safety.

Important legal, organizational and socio-economic measures are taken to ensure environmental safety.
More than 15 laws have been adopted that directly regulate relations in the field of environmental protection and rational use of natural resources, mechanisms and conditions for the use of certain types of natural resources, as well as the procedure for conducting state environmental impact assessments, organizing various categories of protected territories and more than 30 legal acts that define procedures and other issues.

The decree of the President of the Republic of Uzbekistan Shavkat Mirziyoyev of April 21, 2017 “On improving the public administration system in the field of ecology and environmental protection” and the decree “On measures for the radical improvement and development of the household waste management system for 2017-2021” serve to further expand the scope of work in this area [1].

In today's fast-paced world, the use of natural resources by people is increasing day by day. At the moment our main goal is to use natural resources wisely and pass them on to future generations. Therefore, our generations are obliged to deeply process every hydrocarbon extracted from the earth, create non-waste technologies and prevent damage to nature under the influence of various wastes [2, 3].

It is known that the pyrolysis process is based on the production of unsaturated hydrocarbons by decomposition of saturated hydrocarbon gases at high temperatures in an airless place. During ethane pyrolysis in gas-chemical complexes, dimethyldisulfite is added to the feed to prevent coke formation in the pipes of the pyrolysis furnace and water vapor is added to reduce the partial pressure of the process.

In consequence the pyrolysis gas contains acid gases (H_2O and CO_2) and oxygen-containing organic compounds (aldehydes, ketones, acids, alcohols).

The absorption process is carried out to purify the pyrolysis gas. As absorbents, 2% and 10% aqueous solutions of alkali are used. Pyrolysis gas passes through an alkaline treatment column, then acidic gases (H_2O and CO_2) are separated.

Pyrolysis gas purification is carried out in two stages, to achieve a purity of 1 ppm of pyrolysis gas on the acid gas, the pyrolysis gas is first cleaned in the lower part of the column with a “weak” solution with a mass concentration of 2% free alkali. Then the pyrolysis gas is purified in the middle of the column with a solution of free alkali with a mass concentration of 10%. In the column, acidic gases — H_2S and CO_2 — react with alkaline NaOH to form sulfides and carbonates [4].

Organic compounds (aldehydes, ketones, acids, alcohols) in the pyrolysis gas are polymerized by the action of an alkali catalyst NaOH. The mechanism of polymerization processes in an alkaline treatment column is accompanied by aldol condensation of the C=O bond (aldehydes, ketones, acids, alcohols).

As a result, during the purification by pyrolysis gas, a yellow oil is formed in the cubic part of the column (aldol condensation product, polymer). The problem of the formation of waste yellow oil is one of the typical problems of the process of purification of pyrolysis gas with alkali. As a result of contamination of the yellow oil system:

- pollution of the internal components of the column, which leads to a decrease in its effectiveness in the purification of pyrolysis gas from acid gases;
- increased demand for pure alkali;
- an increase in the amount of alkali used, an increase in the amount of utilized effluents;
- pollution of the used alkali with the polymer;
- leads to contamination of the used device for oxidation and neutralization of alkali.

It is not recommended to raise the temperature to a higher value, as this can lead to the precipitation of dissolved salts and cause difficulties in the operation of the alkaline treatment column.

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The waste yellow oil generated in the pyrolysis gas purification device is poured from the cubic part of the oil column into the drums and taken out of the device zone [6]. This waste yellow oil is considered waste products from gas chemical complexes and is not currently used for any purpose. Therefore it is essential to study the composition of these wastes, extract the necessary substances from them, use the separated substances as secondary raw materials, collect waste annually and reduce their damage to the environment and nature.

2. Research methods
The traditional methods of settling, determining the properties of the separated substances, gas separation when heating liquids, sampling gas and determining the gas content using a gas chromatograph are used in the studies. At the initial stage of the study, the physical properties and composition of the yellow oil were determined using several research methods. The first of these was done through interrogation.

2.1. Settling
A distillation process was carried out to separate the oil from the device [7]. The 1-liter laboratory graduated cylinder was filled with 1 liter of oil and given for settled for 24 hours. As a result of the settling, the oil was divided into three layers due to its density. The upper layer is a viscous oily part from yellow to red, the middle layer is a brittle polymer part which is crushed by trapping green grains and the lower layer is a part from yellow to brown with water content. Table 1 shows the volumetric composition of the yellow oil [8].

| Part      | Amount, % (volume) |
|-----------|--------------------|
| Oilypart  | 35                 |
| Polymerpart | 55                |
| Waterpart | 10                 |
| Total     | 100                |

2.2. Determination of the density of the oily part
Several methods have been used experimentally to define the density of substances whose state of aggregation is liquid. These are: Areometric method, Westphal-Mor weighing method, pycnometric method and hydrostatic methods. In this study, the determination of the density of the oily part was carried out in accordance with the requirements of GOST 3900-85. A cylindrical vessel was taken and the oil fraction was placed inside. In a water bath, the temperature was maintained at 20 °C, then the hydrometer was lowered from the center of the vessel and the substance density was determined [9]. The values determined in each method were compared with others and the results were evaluated.

2.3. Determination of the kinematic viscosity of the oily part
One of the most common methods for determining the kinematic viscosity of liquids is the use of viscometers.

In the experiment, the kinematic viscosity of the oily part was determined in accordance with the requirements of GOST 33-2016. The viscometer consists of a U-shaped glass tube, one bend of which is wider, a capillary with a diameter of 0.7-1.0 mm is connected to a thin bend and the top of the capillary consists of a ball with a capacity of 2-3 ml. The upper part of the sphere is narrow and its upper and lower parts are indicated by the letters A and B.

A rubber tube is attached to the end of the ball. During the experiments, a viscometer was installed in the thermostat. The results were obtained with temperature control. The kinematic viscosity of the oily part was determined using an Ostwald-Pinkiewicz viscometer at 20 °C and 40 °C [10].
2.4. **To determine the state of the oily part**

Determination of the environment of substances is used to find out what environment they are in (acidic, neutral and alkaline). Two experiments were conducted to determine the state of the oil fraction.

In the first experiment, the determination of the medium of the oil fraction was carried out by using indicator paper and the color of the indicator paper remained almost unchanged. After that the studies were conducted on a METTLER TOLEDO automatic titrator of the EasyPlus\textsuperscript{TM} series \[12\] in order to get a clear result in the second experiment.

2.5. **Determination of heat capacity of the oily part**

The amount of heat spent on raising the temperature of the system to 1 °C is called the heat capacity of this substance.

The heat capacity of the oil fraction was found by practical calculation. For this, we used the formula for the dependence of the specific heat density of liquid petroleum products. The heat capacity of the oil fraction at temperature $t$ can be calculated by the following formula \[13\]:

$$c = \frac{1}{\sqrt{d_{15}^{15}}} (0,403 + 0,000405t)$$

(1)

The heat capacity of the oil fraction was calculated at 20 °C and 40 °C.

here:

$c$ - is the average heat capacity of the liquid oil fraction, kcal / (kg · deg);

$d_{15}^{15}$ - is the relative density of the oil fraction, $t$ - is the temperature of the oil fraction, 0 °C.

The heat capacity of the oil fraction was calculated at 20 °C and 40 °C.

2.6. **Determination of the molecular weight of the oily part**

The molecular weight of the liquid is determined experimentally by the cryoscopic method. The molecular weight of the liquid product is the average relative molecular weight of the individual substances that make up the complex liquid product. The essence of this method is that the results include proportional to the molecular concentration of the melt of the test product.

Based on the results obtained in the experiment, the molecular weight was calculated by the following formula:

$$M = \frac{A \cdot 5.12 - 1000}{B \cdot t}$$

(2)

here:

$A$ - is the mass of the investigated liquid product, in grams;

5.12 - cryoscopic molecular dispersion of benzene;

$B$ - is the mass of benzene, in grams;

$t$ - the dispersion of the temperature of the solution °C.

The rarefaction temperature of a solution of benzene and liquid hydrocarbons is determined by using a Beckman thermometer. This type is a differential thermometer that measures the change in temperature, not the temperature itself. The results were introduced into the second expression and the molecular weight of the oil fraction was found \[14\].

2.7. **Determination of the refractive index of the oily part**

In practice, the optical properties of liquids - refractive index, molecular refraction, and dispersion - are used to quickly determine the composition and quality control of liquid products.

The light refractive index is used to identify substances and determine their purity. The refractive index of a substance is determined on ABBE refractometers. ABBE refractometers include URL, IRF-22 and Pulfrixa-IRF-23 refractometers. The function of such refractometers is to determine the refractive index directly.
The refractive index of the fractions is determined in mixed products (fractions) on an IRF-22 refractometer at a temperature of 293 K with an accuracy of ± 0.001. In the experiment, the refractive index of the oily part was determined in accordance with the requirements of GOST 5482-90 [15].

2.8. Degassing by heating the oily part and sampling the separated gas
To conduct this experiment, the device shown in Figure 1 was assembled. Initially, the three-necked flask 5 is mounted on a tripod 3. The three-tube flask 5 is tightly attached to the left throat with a glass tube 2 to remove the degassed liquid and the right throat with a gas-tight hose 6 which serves to collect the separated gas from the liquid. The collector flask 1 is located at the outlet of the glass tube 2 for collecting degassed liquid. The funnel nozzle 4 is tightly fixed with a stopper to ensure an uninterrupted supply of fluid to the middle throat of a three-necked flask 5. A container 11 is placed on top of the tripod [16].

Since most gases are soluble in water, a saturated solution of water in sodium chloride is added to container 11 as a gas sampling liquid. This, in turn, prevents the dissolution of gases in a liquid. Test tube 8 is filled with liquids and turned over carefully and fixed on a tripod 10.

When test-tube 8 is turned upside down, check that there is no air on the surface of the internal fluid. Glass tube 9 is connected to hose 6.

Heating magnetic stirrer 7 is installed [17,18] at the bottom of the three-necked flask 5.

![Figure 1](image)

**Figure 1.** Division of dissolution of gases in a liquid and an equipment for a gas sampling.
1 - prefabricated flask; 2 and 9 - glass tubes; 3 and 10-tripods; 4- dropping funnel; 5- three-necked flask; 6- gas hose; 7-heating magnetic stirrer; 8-test tube; 11- container.

2.8.1. The course of the experiment. The yellow oil obtained from the device was poured into the flask until one third of the middle neck of flask 5 with three hoses was empty and then a steel rod was placed in the flask for stirring.
A dropping funnel was mounted on funnel 4, three-wheeled flask 5 with a cork and oil was poured into it. A glass tube 9 was immersed in a liquid sauce 11 filled with liquid in a proofing tube 8.

The heating magnetic stirrer 7 was connected to an electric current, the liquid in the three-necked flask 5 was heated to 70 °C with slow stirring and this temperature was maintained until the end of the experiment. As a result, the gas began to separate from the glass tube 9. Gas was removed from the glass tube 9 which was immersed in the liquid for three minutes.

This was done to ensure that the air in the flask and hose and the gas saturation of the liquid in the vessel 11. When the amount of waste gas through the glass tube 9 decreased, the tap of dropping funnel 4 was opened and yellow oil was poured into the three-necked flask 5.

The oil flow rate was controlled inversely with the speed of the gas that exited the tube. The degassed liquid began to flow through the glass tube 2 in a three-necked flask 5 and was collected in the collector 1. Thus, the experiment continued until the necessary gas was obtained.

After collecting the required amount of gas in test tube 8, the test-tube was tightly closed by leaving a certain amount of liquid in the mouth with the help of a stopper, and marked as gas that was obtained from yellow oil.

The separation of gas from the oil part was also carried out in the above sequence and the resulting gas solution was recorded as gas from the oil part.

2.9. Determination of the chemical composition of the resulting gas

The chemical composition of the obtained gas samples was determined on an AGILENT gas chromatograph in accordance with the requirements of GOST 31371.1-2008 [18].

2.10. Determination of the physical properties of the resulting gas

The physical properties of the obtained gas samples were determined in accordance with the requirements of GOST 31369-2008 [19].

 Obtained results and analyzes.

Some important physical characteristics of the oily part of the waste oil formed during the purification of pyrogas in gas chemical complexes were revealed in our study. The physical parameters of the oil part identified as a result of the study are shown in table 2.

**Table 2. The experimental parameters of the oily part.**

| Name of indicator                                    | Unit of measurement | The determined value of the indicator |
|-----------------------------------------------------|---------------------|--------------------------------------|
| Appearance                                          | –                   | Yellow to reddish viscous oil         |
| Density at 200 °C                                   | kg / m³             | 971                                  |
| Relative density, \(d_{20}^{4}\)                     | –                   | 0.971                                |
| Relative density, \(d_{15}^{20}\)                   | –                   | 0.974                                |
| Kinematic viscosity at 20 °C                        | mm²/s - kcal / (kg · deg) kcal / (kg · deg) | 27.958                              |
| Kinematic viscosity at 40 °C                        | mm²/s              | 12.498                               |
| Hydrogen Index (pH)                                 | –                   | 6                                    |
| Heat capacity at 20 °C                              | kcal / (kg · deg)   | 0.4165                               |
| Heat capacity at 40 °C                              | kcal / (kg · deg)   | 0.4247                               |
| Molecular weight                                    | g / mol             | 742                                  |
| The light refractive index of the oil fraction       | \(n_D^{20}\)        | 1.547                                |
In addition, the dissolved gases in the waste yellow oil and the oily part obtained from it were separated. The chemical composition of the recoverable gases and some physical parameters were determined. The chemical composition of the gas samples obtained as a result of the study are shown in Table 3.

**Table 3.** The chemical composition of the waste yellow oil and gas, made from the extraction of oily part is determined on an AGILENT gas chromatograph.

| Component Name | Derived from Yellow Waste Oil | Taken from the oily part |
|----------------|-------------------------------|--------------------------|
| Methane        | 22.67                         | 27.72                    |
| Ethane         | 3.56                          | 0.00                     |
| Propane        | 3.11                          | 2.37                     |
| n - Bhutan     | 0.00                          | 0.00                     |
| i - Bhutan     | 40.89                         | 41.70                    |
| i - Pentane    | 0.44                          | 0.71                     |
| n – Pentane    | 2.22                          | 1.90                     |
| Hexane         | 27.11                         | 25.6                     |
| **Total amount:** | 100                           | 100                      |

Determination of the chemical composition of a mixture of hydrocarbon gases extracted from waste oil and its extracted oil part which will allow us to conduct further research, its use and separation of ethane gas which is less expensive than natural gas components and the production of various products. It is also useful for determining how effective or ineffective the use is.

From table 3 it is seen that the largest share in both gas samples corresponds to butane which is a gaseous state under these normal conditions. This indicates that when gas is used as fuel, it forms a fully combustible mixture with air and can produce high thermal energy.

Furthermore, using a specific chemical composition of gas in accordance with the requirements of GOST 31369-2008, it was divided into the determination of some important physical parameters in this study. The physical properties of the obtained gas samples, determined at a temperature of 20 °C and a pressure of 101.325 kPa, are shown in table 4.

**Table 4.** Some indicators of waste yellow oil and gases released from settled oil.

| Component Name           | Derived from Yellow Waste Oil | Taken from the oily part |
|--------------------------|-------------------------------|--------------------------|
| Density at 20 °C, (kg / m³) | 2.291                         | 2.231                    |
| Relative density 20 °C   | 1.903                         | 1.853                    |
| Molecular mass           | 55.127                        | 53.674                   |
| High heat of combustion, (kJ / mol) | 2735.441               | 2666.586                 |
| Low heat of combustion, (kJ / mol) | 2523.768               | 2459.496                 |
| High heat of combustion, (kJ / kg) | 49620.712              | 49681.148                |
| Low heat of combustion, (kJ / kg) | 45780.978               | 45822.856                |
| High heat of combustion, (kJ / m³) | 113981.051              | 110838.641               |
| Low heat of combustion, (kJ / m³) | 104884.221              | 102230.792               |
| Critical temperature, K   | 389.165                       | 380.701                  |
| Critical pressure, kPa    | 3806.719                      | 3817.041                 |

From the analyzes studied above it can be seen that the concentration of alkali in gas-chemical complexes during alkaline purification of pyrogas does not exceed 15% and the operating temperature
does not exceed 43 °C which is the most important factor for the process. It should be noted that an increase in temperature in the process from 43 °C leads to the precipitation of dissolved salts and the formation of a polymer with a relatively high molecular weight which causes difficulties in the operation of the alkaline treatment column.

The results of the study show that the presence of a certain amount of dissolved hydrocarbon gases in the waste oil generated and recovered in the device indicates that it is a source of ready energy.

It was discovered that a certain amount of combustible gases could be lost and these gases could be harmful to nature if we separate the waste oil directly. From table 4 it can be seen that the high heat of combustion of 68855 joules and the lower heat of combustion of 64,272 joules give more energy during the combustion of a mole of gas extracted from waste yellow oil than in a gas separated from the oily part.

The results show that the energy released during the combustion of 1 m³ of gas from the waste oil is equal to the energy of combustion of a mixture of 2.8 m³ of natural gas and 1.06 m³ of propane-butane (ratio 0.7:0.3).

3. Conclusion

It was found that the most optimal and effective method for the initial separation of the waste oil generated during the purification of pyrogas is the precipitation method. The studies have shown that when settling waste yellow oil for 24 hours, separation efficiency of 90% can be achieved.

The physical properties of the oily part which is settled as a result of the extraction of yellow oil are determined. The necessary information was obtained for the calculation of equipment and devices intended for the processing of the oily part.

Degassing the waste yellow oil formed in gas chemical complexes immediately after installation at a temperature of 70 °C will allow us to obtain additional gaseous fuel for process furnaces and prevent the spread of hydrocarbon gases that pollute degassed oil more than before.

Moreover, mineral salts of waste oil mixed with oil and polymer components at 70 °C improve the solubility of water in the waste oil and the decomposition of emulsions between oil and water which in turn accelerates the decomposition of degassed waste oil.

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