INTRODUCTION

There is growing interest in the ethanol production from abundant and low-cost waste, for example, agricultural waste [Kim and Dale, 2004; Reijnders, 2008; Sarkar et al., 2012], municipal solid waste and food waste [Ma et al., 2017; Yan et al., 2011] in the modern world. Among these low-cost substrates, municipal solid waste is an abundant raw material with zero cost; due to the excessive concentration of population in cities and the emergence of metropolises, the waste situation is becoming acute. In terms of municipal solid waste disposal methods, waste landfilling is characterized by the maximum practical distribution in the world practice, but judging by the experience of waste management of the leading countries of the world, disposal of wastes using this method at the present time becomes unpromising, since it pollutes the territories and groundwater [Nozhevnikova, 2016].

It should be noted that various factors, including culture, location, weather conditions, as well as the degree of economy and development of a given society, affect the composition of municipal solid waste [Alavi Moghadam et al., 2009]. Solid waste generated in developing countries every year, contains 40–88% food waste [Sharholy et al., 2007; Talyan et al., 2008; Yousuf and Rahman, 2007], indicating that the organic fraction of the waste consists mainly of starch, lignocellulose, and lipids. Starch and lignocellulose have a high potential for conversion to ethanol, while other organic fractions such as lipids cannot be converted to ethanol, but these biodegradable components can be converted to biogas by anaerobic fermentation. Pretreatment can increase the bioavailability of lignocellulose by the cellulase. Among the various methods, hydrothermal pretreatment reduces the formation of fermentation inhibitors, which are formed mainly by sugar degradation. Hydrothermal pretreatment is an
environmentally friendly process because it uses no chemicals; this treatment removes most of the hemicellulose and improves the enzyme availability for cellulose [Taherzadeh and Karimi, 2008].

MATERIALS AND METHODS

Fractional models of organic components, which were collected in accordance with the approximate chemical composition of municipal solid waste, were used in this qualitative research implementation, as well as a sample with organic components from the municipal solid waste landfill of the “Tartyp” Joint Stock Company (JSC), Almaty. A total of 5 fractions with various composition and mass were collected:
- Natural sample from the municipal solid waste landfill of Almaty (1500 g);
- lipids containing model fraction (509 g);
- Cellulose containing model fraction (850 g);
- Carbohydrates containing model fraction (900 g);
- Combined fraction (cellulose – 850 g, carbohydrates – 900 g, lipids – 500 g).

The experimental procedure consists of the following main stages: preliminary hydrothermal treatment, enzymatic hydrolysis (amylase, glucavamarin, amylosubtiline, cellulase), ethanol fermentation (alcohol yeast) of the liquid waste fraction.

The sample was formed, moisture content and pH were determined, and then it was hydrothermally treated at 120°C for 4 hours. Qualitative reactions for the presence of starch and glucose were carried out after hydration, then the samples were separated into liquid and solid fractions and the fermentation began. Afterwards, 1.5 gamylosubtilin was added to the liquid part of the sample for 1.5 hours at 65°C, then 2 g of glucavamarin for 1.5 hours at 50°C. Subsequently, 2 g of cellulase was added to the solid part of the sample for 1.5 hours at 50°C and 1.5 g of amylase at 65°C for 1.5 hours. The fermentation was followed by ethanol fermentation, for this purpose alcoholic yeast (15 g) is added to the liquid part for ethanol production [Mahmoodia et al., 2018].

RESULTS AND DISCUSSION

In the qualitative research, liquids with various volumes were obtained from each model sample after hydrothermal pretreatment, fermentation, and ethanol fermentation.

The obtained samples with liquids were analyzed by Gas chromatography–mass spectrometry (GC-MS) (Agilen 7890A \ 5975C) to determine the chemical composition. Passing through the chromatograph, the samples are separated into components, and the mass spectrometer is responsible for their identification and analysis. This detection mode is highly accurate, its essence is to record readings not over the total volume of the incoming ion current, but over the maximum ions for the supposed molecules, and curves of the time dependent signal are plotted. The chromatogram is a graphical representation of the detector signal used to measure the concentration of substances in the eluate, from the time of the mobile phase. Schematically, chromatograms are the Gaussian peaks sequence on a baseline.

The analysis of the model combined sample detected the presence of the following components in the composition: ethanol, 1-butanol, 3-methyl, propanoic acid, 2-methyl, oxime, methoxy-phenyl, and l-α- terpineol. Table 2 provides the data on retention time, peak areas and components, abundance and concentration of these substances.

In accordance with Table 2, a graph of gas chromatography–mass spectrometry was provided, which shows the result of recording the time dependent abundance at the column outlet. The concentration of each peak in percent is calculated from the peak area. Table 3 shows the results of gas chromatography analysis of the lipids containing sample, with the following composition of this sample: ethanol, 1-butanol, 3-methyl, propanoic acid, 2-methyl, butanoic acid, butyric acid, 3-methyl, oxime,
methoxy-phenyl, pyrazine, tetramethyl, phenyl-ethyl alcohol, triethyl citrate, phthalic acid, and butyl hex-3-yl ester. The retention time required to elute the substance corresponds to the time of the peak maximum appearance on the chromatogram, the peak areas, the abundance or signal of the detector, as well as the data on the substances percentage in the sample.

Table 1. Ethanol fermentation results

| No. | Sample Name and mass (g)                                                                 | The amount of liquid after ethanol fermentation (ml) |
|-----|----------------------------------------------------------------------------------------|-----------------------------------------------------|
| 1   | Natural sample from the municipal solid waste landfill of Almaty (1500 g)               | 135 ml                                              |
| 2   | Lipids containing model fraction (509 g)                                               | 80 ml                                               |
| 3   | Cellulose containing model fraction (850 g)                                            | 117 ml                                              |
| 4   | Carbohydrates containing model fraction (900 g)                                        | 95 ml                                               |
| 5   | Combined fraction (cellulose - 850g, carbohydrates - 900g, lipids - 500g)              | 162 ml                                              |

Table 2. Components of the combined sample

| Peak No. | Ret time (min) | Area (S)   | Component                           | Abundance | %    |
|----------|----------------|------------|-------------------------------------|-----------|------|
| 1        | 1.681          | 4237936015 | Ethanol                             | 94        | 95.8 |
| 2        | 3.978          | 151571481  | 1-Butanol, 3-methyl-                | 62        | 3.4  |
| 3        | 6.389          | 3217162    | Propanoic acid, 2-methyl-           | 73        | 0.1  |
| 4        | 9.499          | 28243644   | Oxime-, methoxy-phenyl-             | 77        | 0.6  |
| 5        | 17.185         | 2258941    | L-α-Terpineol                       | 71        | 0.1  |

Figure 2. Chromatogram of the time (time) dependent components concentration of the combined sample (abundance)
The lipid sample contains characteristic aromatic heterocyclic organic compounds in its component composition, such as Pyrazine, monobasic short-chain saturated fatty acids (Butyric acid), and monohydric phenylethyl alcohol contained in essential oils, which indicates the reliability of the analysis method.

According to the data in Table 3, the provided chromatogram clearly shows the dependences of the components abundance and the retention time (the time required for substance elution corresponds to the time of the maximum peak appearance in the chromatogram). Each peak with the corresponding number reflects the component presented in the table.

The results of the mass spectrometry analysis of the sample with cellulose detected the following components concentrations: ethanol, 1-butanol, 3-methyl oxime, methoxy-phenyl, and dibutyl phthalate. This sample showed the lowest percentage of ethanol, compared to the others, since cellulose contains ligninocellulose in its

Table 3. Concentration of the lipids containing sample components

| Peak No. | Ret time (min) | Area (S)   | Component                        | Abundance | %   |
|---------|----------------|------------|----------------------------------|-----------|-----|
| 1       | 1,733          | 2084267735 | Ethanol                          | 93        | 93.85 |
| 2       | 3,974          | 66427254   | 1-Butanol, 3-methyl-              | 81        | 2.99  |
| 3       | 6,623          | 3468608    | Propanoic acid, 2-methyl-         | 83        | 0.16  |
| 4       | 7,407          | 4610257    | Butanoic acid                    | 77        | 0.21  |
| 5       | 8,522          | 10123063   | Butanoic acid, 3-methyl-          | 63        | 0.46  |
| 6       | 9,576          | 31078988   | Oxime-, methoxy-phenyl-           | 85        | 1.40  |
| 7       | 15,176         | 9813476    | Pyrazine, tetramethyl-            | 80        | 0.44  |
| 8       | 16,477         | 9109129    | Phenylethyl Alcohol              | 74        | 0.41  |
| 9       | 27,674         | 1155125    | Triethyl citrate                  | 75        | 0.05  |
| 10      | 33,817         | 909606     | Phthalic acid, butyl hex-3-yl ester | 77        | 0.04  |

Figure 3. Graph of the lipids containing sample components ratio
composition, which has a dense structure. Lignin is a complex molecule consisting of phenylpropane units linked in a three-dimensional structure, which is especially difficult to biodegrade, the higher the lignin fraction, the higher the chemical and enzymatic degradation resistance.

Figure 4 shows the graph of the time (peak) dependent detector signal (substance abundance) in the cellulose containing sample. Each component corresponds to the time and peak registering the detector response.

In the sample with carbohydrates, after analysis on the gas chromatograph, the content of ethanol (96.27%) was detected; the sample also contains such components as: 1-butanol, 3-methyl, oxime, and methoxy-phenyl.

The chromatogram of the carbohydrates containing model sample is shown in Figure 5, where each component corresponds to the peak number and retention time.

A natural sample from the municipal waste disposal landfill of Almaty, after a qualitative research with fermentation, showed the highest ethanol content of 97.45% compared to other samples, as well as such substances as oxime-, methoxy-phenyl, ethyl 2- (5-methyl-5-vinyltetrahydrofuran-2 –yl), propan-2-yl carbonate, pyrazine, tetramethyl, 2h-pyran-3-ol, 6-ethenyltetrahydro-2,2,6-trimethyl, and α-terpineol. Table 6 shows the peak time, the area and the abundance of each component, and the concentrations of these substances.

The chromatogram of the substances abundance, the peaks area and the retention time of the sample with the organic fraction of the municipal solid waste landfill in Almaty is shown in Figure 6.

| Peak No. | Ret time (min) | Area (S)     | Component                        | Abundance | %    |
|---------|----------------|--------------|----------------------------------|-----------|------|
| 1       | 1,718          | 2571350344   | Ethanol                          | 92        | 90.84|
| 2       | 3,986          | 201445006    | 1-Butanol, 3-methyl-             | 81        | 7.12 |
| 3       | 9,513          | 37545433     | Oxime-, methoxy-phenyl-          | 79        | 1.33 |
| 4       | 33,818         | 20161521     | Dibutyl phthalate                | 96        | 0.71 |

Figure 4. Chromatogram of the dependence of the substances concentration and the time of the cellulose containing sample.
Table 5. The carbohydrates containing sample components concentration

| Peak # | Ret Time(min) | Area(S)       | Component                   | Abundance | %    |
|--------|---------------|---------------|-----------------------------|-----------|------|
| 1      | 1,715         | 3312233598    | Ethanol                     | 93        | 96.28|
| 2      | 4,215         | 88291610      | 1-Butanol, 3-methyl-         | 69        | 2.57 |
| 3      | 9,497         | 39044278      | Oxime-, methoxy-phenyl      | 79        | 1.15 |

CONCLUSIONS

Ethanol is present in large amounts in all analyzed samples; butanol is also present in the composition, which indicates that pretreatment, fermentation and ethanol fermentation had a positive effect on the bioethanol production. The ethanol concentration in a natural sample obtained from the landfill has the highest rate of 97.45%, compared to the others, which indicates that the natural sample of municipal solid waste from the landfill in Almaty has the greatest potential for its production. Model samples with different homogeneous and heterogeneous composition and also a natural sample from the landfill were selected to assess the differences in the degree of fermentation and ethanol concentration. On the basis of the results, it can be judged that the combination of components and a heterogeneous composition like in the natural waste sample, may contribute to increase the ethanol concentration and its other isomers. Probably, the mixed raw materials contain more components and the effect of enzymes improves their bioavailability and prepares them for ethanol fermentation, and pretreatment promotes the cleavage of lignin and
lignin containing cellulose, which are present in many components of municipal solid waste.

The experiment was carried out under laboratory conditions with small masses of samples, after obtaining ethanol, on an industrial scale, there will be a large amount of residues of the solid part of the waste, which can be exposed by the method of anaerobic fermentation for methane production and its further use as an alternative source of energy, which in its the queue has a good economic benefit, since the waste raw materials have zero cost. Therefore, high concentration Ethanol, as well as biogas (methane) can be produced jointly from organic components of municipal

| Peak No. | Ret time (min) | Area(S)   | Component                                               | Abundance | %     |
|----------|----------------|-----------|---------------------------------------------------------|-----------|-------|
| 1        | 1.731          | 2339904556| Ethanol                                                 | 91        | 97.45 |
| 2        | 9.559          | 44417720  | Oxime-, methoxy-phenyl-                                | 80        | 1.85  |
| 3        | 14.317         | 5705926   | Ethyl 2-(5-methyl-5-vinyltetrahydrofuran-2-yl)propan-2-yl carbonate | 86        | 0.24  |
| 4        | 15.18          | 7123396   | Pyrazine, tetramethyl-                                 | 81        | 0.30  |
| 5        | 16.779         | 2328081   | 2H-Pyran-3-ol, 6-ethenyltetrahydro-2,2,6-trimethyl-    | 63        | 0.10  |
| 6        | 17.185         | 1557327   | α-Terpineol                                            | 67        | 0.06  |

Figure 6. Graph of the natural sample components concentration obtained from the municipal solid waste landfill of the “Tartyp” Joint Stock Company (JSC) in Almaty
solid waste. In addition to the direct economic benefit, the production of biogas and bioethanol from waste can:
- reduce the waste sites volume;
- reduce greenhouse gas emissions;
- reduce the natural gas consumption.

It is necessary to develop alternative energy to support the global efforts to reduce the greenhouse gas emissions and improve the climate by producing ethanol and methane from the organic fraction of municipal solid waste.

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