Klaipeda University

Alternative fuels

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INTRODUCTION

According to the U.S. Energy Information Administration’s (EIA) International Energy Outlook 2014, the global supply of crude oil, other liquid hydrocarbons, is expected to be adequate to meet the world's demand for liquid fuels for at least the next 25 years. So the world should think about Alternative fuels, Regarding this alternative fuel the research are keep going on this area and lot of ways available like renewable energies.

INTRODUCTION

Roadmaps towards sustainable bioeconomy, including the production of biofuels, in many EU countries mostly rely on biomass use. However, although biomass is renewable, the efficiency of biomass production is too low to be able to fully replace the fossil fuels. The use of land for fuel production also introduces ethical problems in increasing the food price.

INTRODUCTION

Biofuels are liquid or gaseous transport fuels such as biodiesel and bioethanol which are made from biomass. They serve as a renewable alternative to fossil fuels in the EU's transport sector, helping to reduce greenhouse gas emissions and improve the EU's security of supply. By 2020, the EU aims to have 10% of the transport fuel of every EU country come from renewable sources such as biofuels. Fuel suppliers are also required to reduce the greenhouse gas intensity of the EU fuel mix by 6% by 2020 in comparison to 2010.

INTRODUCTION

Depending on the origin and production technology of biofuels, they are generally called as the **first, second and third** generation biofuels (according to the EASAC report 2012), while the fourth generation biofuels make use of novel synthetic biology tools and are just emerging at the basic research level

THE FIRST GENERATION BIOFUELS

The most of the first generation biofuels are sourced from crop plants as energy-containing molecules like sugars, oils and cellulose. They provide only limited biofuel yields and have a negative impact on food security. Efforts are now needed to accelerate the generation of advanced biofuels by identifying and engineering effective non-food feedstocks, improving the performance of conversion technologies and the quality of biofuels.

THE FIRST GENERATION BIOFUELS

Most common first-generation biofuels include:

- Biodiesel - extraction of vegetable oils, with or without esterification, from the seeds of plants like soybean, rape (canola) and sunflower
- Ethanol - fermentation of simple sugars from sugar crops (sugarcane) or starch crops (corn, wheat)
- Biogas - anaerobic fermentation of organic waste and crop residues as energy crops

THE SECOND GENERATION BIOFUELS

The second generation biofuels are already an improvement in producing biofuels from feedstock of lignocellulosic, non-food materials that include straw, bagasse, forest residues and purpose grown energy crops on marginal lands.

THE THIRD GENERATION BIOFUELS

The third generation biofuels are based on algal biomass production. They are presently under extensive research in order to improve both the metabolic production of fuels and the separation processes in bio-oil production to remove non-fuel components and to further lower the production costs.

THE THIRD GENERATION BIOFUELS

Algae can produce such fuels:

- biodiesel,
- butanol,
- gasoline (petrol),
- ethanol,
- even jet fuel

EUROPEAN POLICY

Growing biofuels on existing agricultural land can displace food production to previously non-agricultural land such as forests. Because trees absorb CO_2 from the atmosphere, removing them for biofuel production may result in an increase in net greenhouse gases instead of a decrease. To combat indirect land use change, new rules came into force in 2015 which amend the legislation on biofuels – specifically the Renewable Energy Directive and the Fuel Quality Directive.

FUEL QUALITY DIRECTIVE

DIRECTIVE (EU) 2015/1513 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 9 September 2015 amending Directive 98/70/EC relating to the quality of petrol and diesel fuels and amending Directive 2009/28/EC on the promotion of the use of energy from renewable sources http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32015L1513&from=EN

Advanced biofuels, such as those made from wastes and algae, provide high greenhouse gas emission savings with a low risk of causing indirect land-use change, and do not compete directly for agricultural land for the food and feed markets.

BIOFUEL SUSTAINABILITY

Sustainability criteria:

- Greenhouse gas emissions must be at least 35% lower than from the fossil fuel they replace. From 2017, this will increase to 50% and, from 2018, the saving must be at least 60% for new installations;
- The raw materials for biofuels cannot be sourced from land with high biodiversity or high carbon stock.
- The greenhouse gas intensity of fuels is calculated on a life-cycle basis;
- The 6% reduction target is likely to be achieved through the use of biofuels, electricity, the use of less carbon intense, often gaseous, fossil fuels and a reduction of flaring and venting at the extraction stage of fossil fuel feedstocks.

LIST OF SUSTAINABLE FEEDSTOCKS

- Agricultural residues
- Forest biomass
- Energy crops -
- Other biowaste streams
- Algae/Aquaculture

ALGAE

Algae are a very promising source for renewable energy production since it can fix the greenhouse gas (CO_2) by photosynthesis and does not compete with the production of food.

Algae live in a wide range of aquatic environments and are a natural component of most aquatic ecosystems. Aquatic algae are found in both fresh and marine waters.

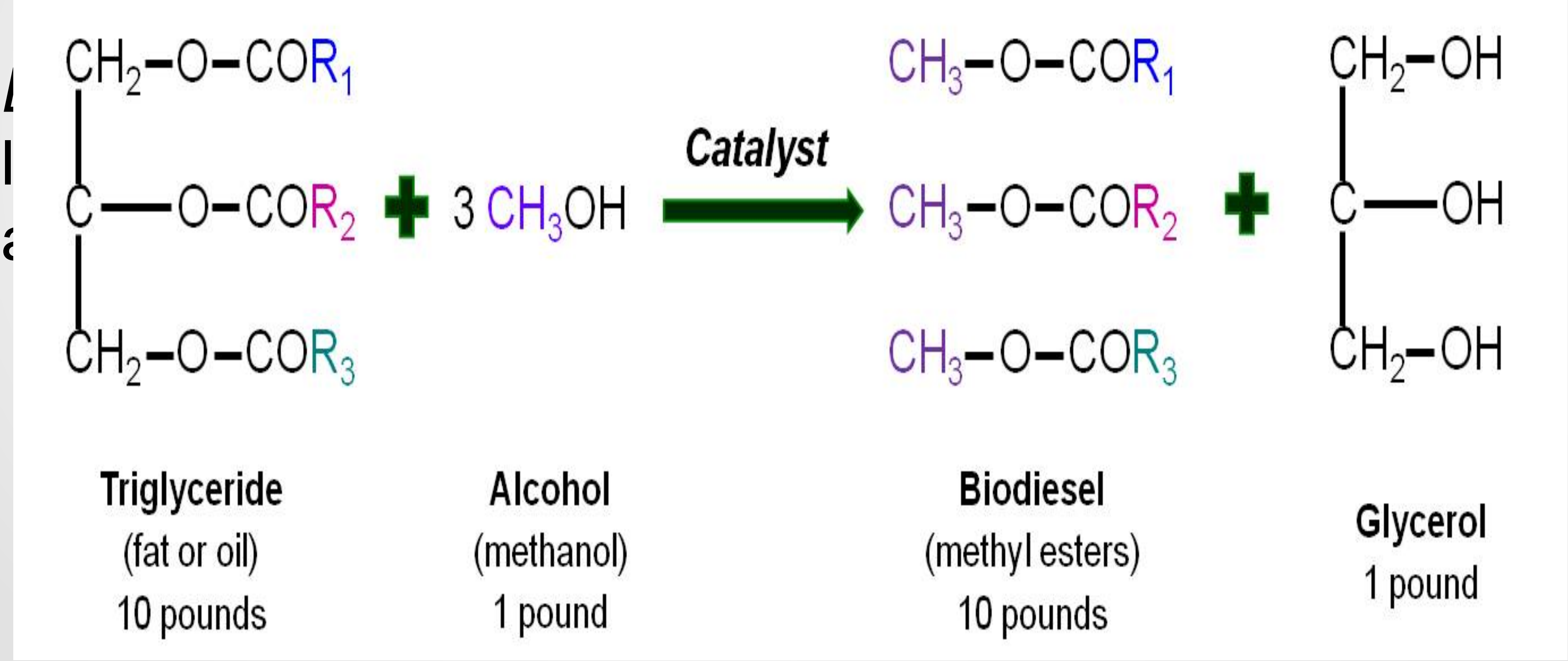
Macroalgae denotes multicellular algae that are visible by eye. The main groups of marine macroalgae are traditionally named by their colour as brown, red, and green macroalgae

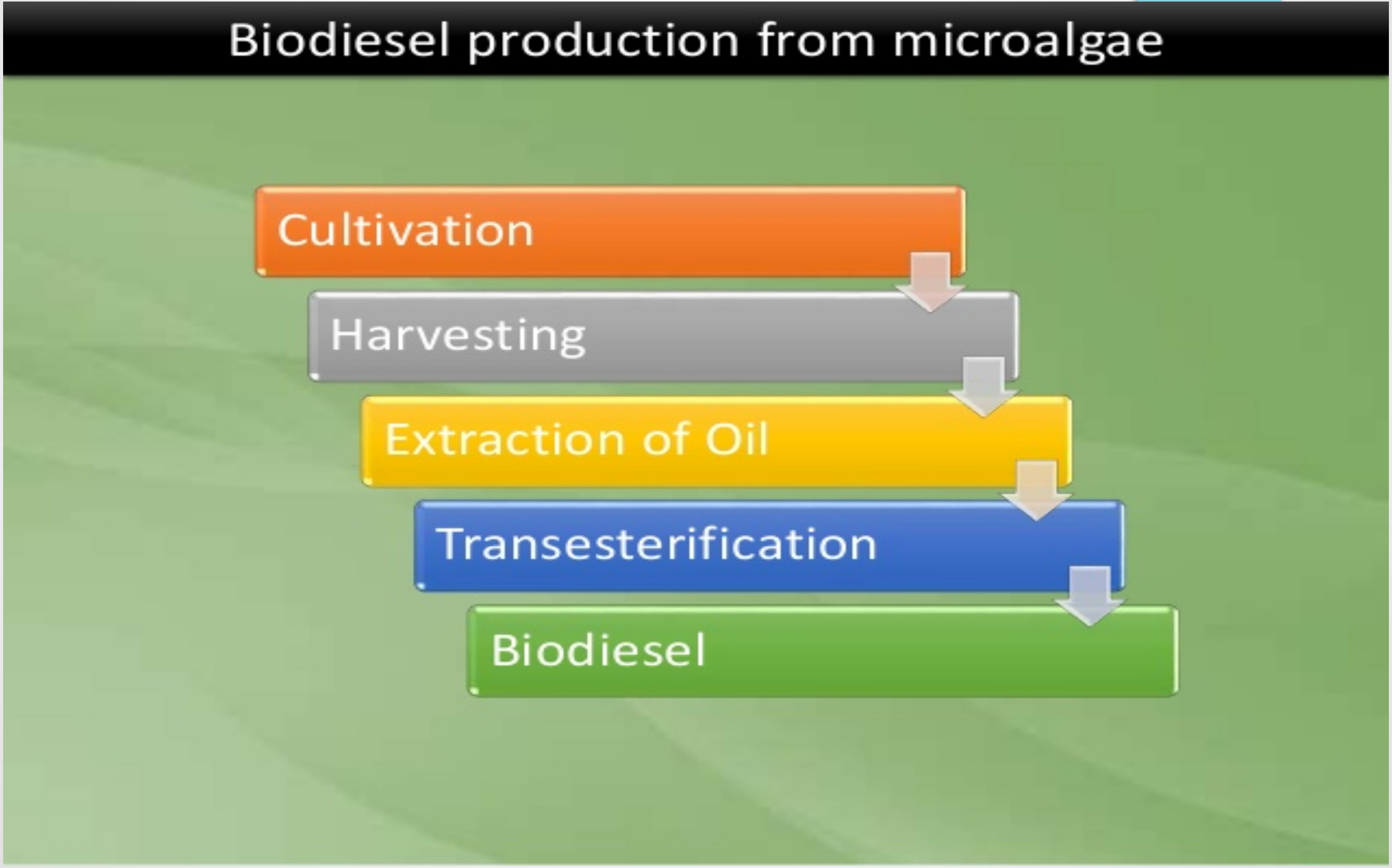
Brown algae *Paeophyta* (Suzanne, 2009)
Red algae *Rhodophyta* (Peter South wood, 2012)
Green Algae *Chlorophyta* (Druehl, 2000)

TYPES OF BIOFUELS FROM MACRO ALGAE

Source	Process	Fuel
Seaweed/ Macroalgae	Anaerobic Digestion	Methane
	Fermentation	Ethanol
	Transesterification	Biodiesel
	Pyrolysis/ Gasification	Hydrocarbons and derivatives

BIODIESEL FROM MACROALGAE




Biodiesel production from microalgae
Cultivation
Harvesting
Extraction of Oil
Transesterification
Biodiesel

BIODIESEL FROM MACROALGAE

The aim of the research was to evaluate the potential of the use of algae biomass in biodiesel production

Tasks:

1. Analyze algae biomass production and biodiesel production technologies
2. Determine the amount of lipids in different types of algae.
3. Perform lipid transesterification using KOH catalyst and different alcohols
4. To investigate the physical and chemical properties of methyl, ethyl and butyl and fatty acids esters. (biodiesel)

BIODIESEL FROM MACROALGAE

Chladophora

Lemnaceae

Pithophora

OIL EXTRACTION

PROCEDURE (according to the standard LST EN ISO 659:2000)

1. The sample is weight on analyticalbalance.
2. The sample is mix with anhydrous sodium sulfate using a ratio 4:1.
3. 150 mL of Hexane is poured into 250 mL round-bottomed flask with boiling chips.
4. Soxhlet apparatus is set for the extraction.
5. After about an hour of extraction, the round-bottomed flask is heated in the water bath of the concentrator apparatus.
6. The solvent is removed and the excess water outside the flask is dried.
7. The extracted fat is weight and the fat content of the sample is calculated.

OIL EXTRACTION

Amount of fat, ml	Amount of KOH catalyst, g	Ester	alcohol	Amount of alcohol, ml	reaction temperature, °C
200	1,8	FAME	methanol	51	55
		FAEE	ethanol	75	68
		FABE	butanol	114	108

CALCULATION

$$\text{FAEyeld} = \frac{V_{\text{eksp}}}{V_{\text{teor}}} \cdot 100\%$$

$$V_{\text{teor.}} = \frac{3 \cdot \left(\frac{V_{\text{lipid}} \cdot \rho_{\text{lipid}}}{M_{\text{lipid}}}\right) \cdot M_{\text{biodyz}}}{\rho_{\text{biodyz}}}$$

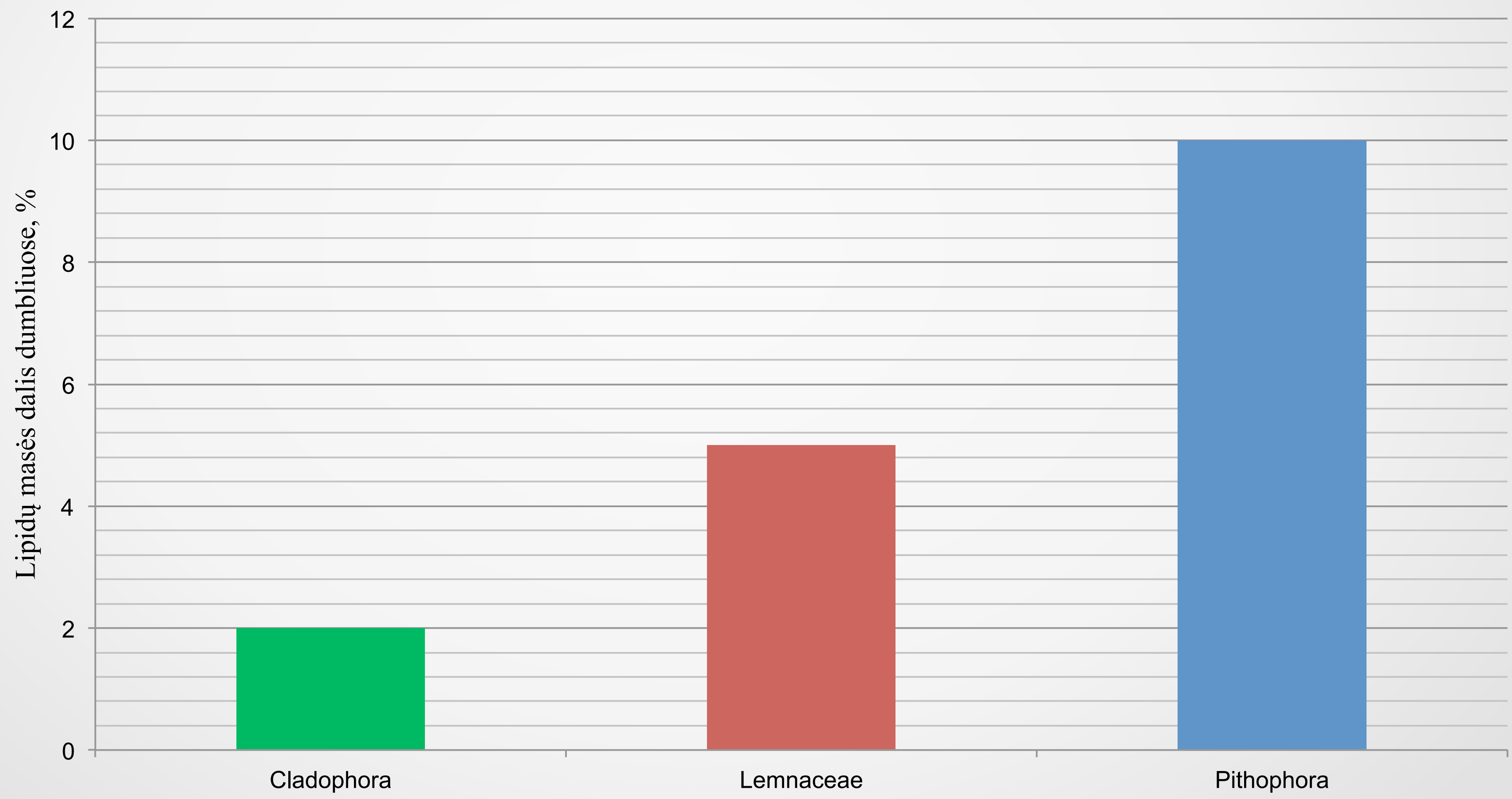
ANALYSIS OF PROPERTIES

Automatic oxidation stability analyzer "Petro OXY"

- Density (LST ISO 758:1997)
- Vicosity (LST EN ISO 3104);
- Oxidative stability (ASTM D7525);
- Calorific value

IKA C5000 calorimeter

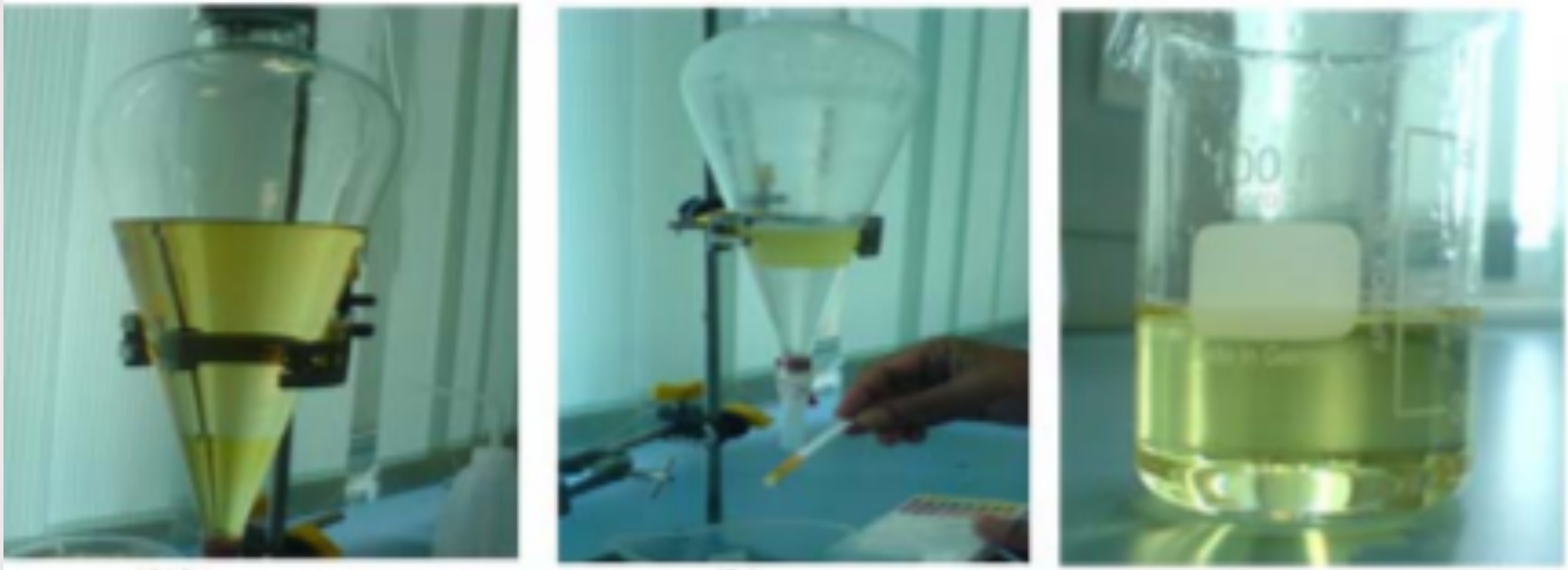
RESULTS



12
10
8
6
4
2
0
Lipidų masės dalis dumbliuose, %
Cladophora
Lemnaceae
Pithophora

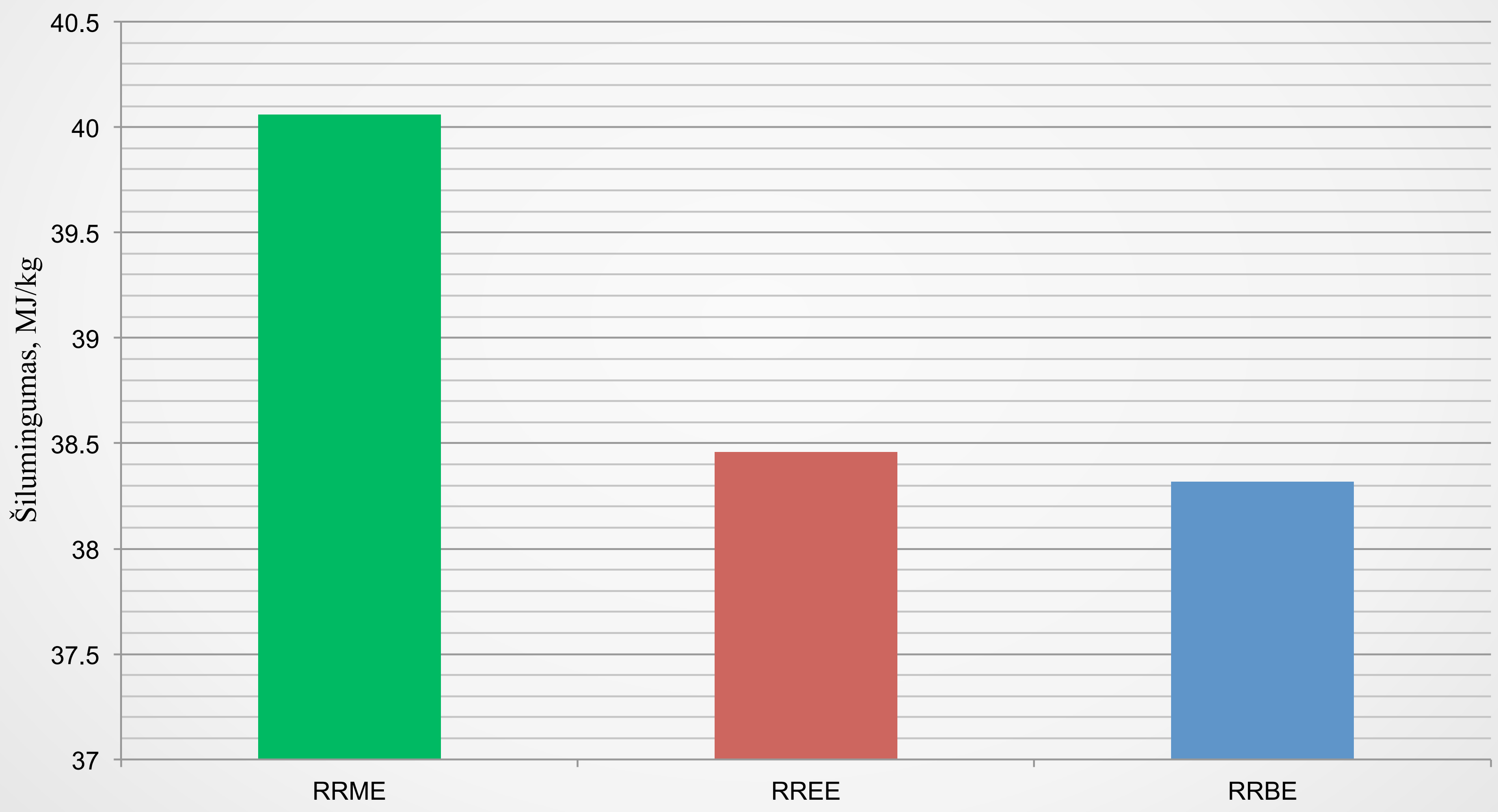
Alcohol	Amount of ester, ml	Amount of glycerol, ml	Yeld, %
methanol	205	41	97
ethanol	201	73	92
butanol	198	107	84

RESULTS



(a) (b) (c)

Pure biodiesel after purification



Šilumingumas, MJ/kg
40.5
40
39.5
39
38.5
38
37.5
37
RRME
RREE
RRBE

SUMMARY

Research was to perform the reaction of Pithophora lipids transesterification by using different alcohols (methanol, ethanol and butanol) and evaluate the phisco-chemical properties of derived metyl, etyl, and butyl esters. Results were compared wih LSTEN14214 biodiesel standart requirements. All ester satisfy density requirements, only metyl ester meet the lower viscosity requirements of 5,0 $mm^{2.}$ /s. None of the esters meet oxidation stability requirements. Etyl and butil esters can be used alone during summer.

PRODUCTION OF ALTERNATIVE FUELS FROM MACRO-ALGAE

Nowadays there is increase in fossil fuel consumption. Due to that demand, fossil fuel reserves are depleting very fast, so there is a need for alternative fuels. Many scientist are focusing on biofuel production from biomass. Many technologies can convert biomass to biofuels. One of them is pyrolysis. Most promising biomass is considered algae because they grow very fast and do not need many investments.

PYROLYSIS PROCESS

Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen (or any halogen). It involves the simultaneous change of chemical composition and physical phase, and is irreversible

PYROLYSIS PROCESS

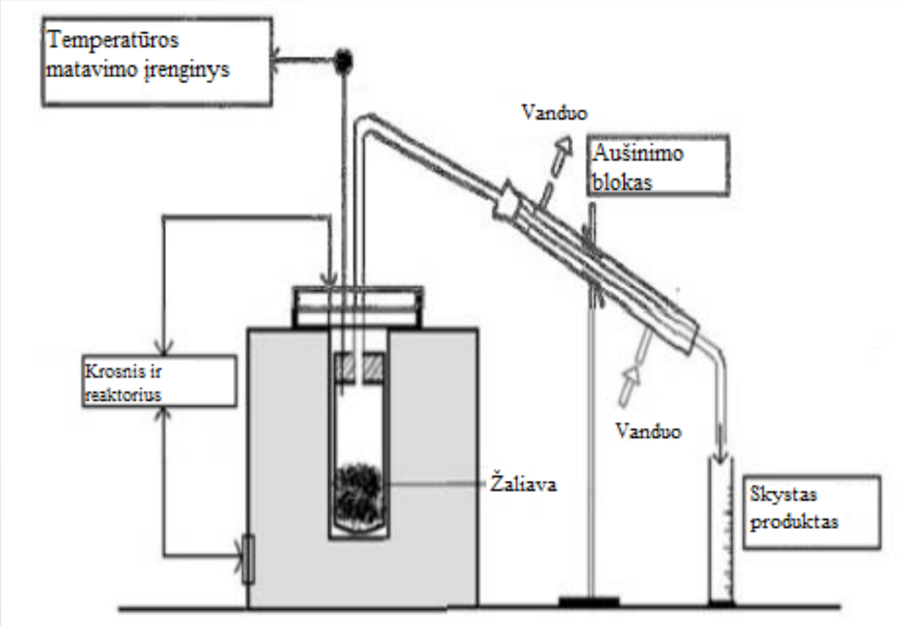
Pyrolysis process	Residence time, s	Rate of rising temperature, °C/s	particle size, mm	Temperature, °C	Yields of products, %		
					Bio-oil	Char	Gas
Slow	300-1800	<50	5-50	300-600	30	35	35
Fast	<5	>200	<1	400-700	50	20	30
Flash	<0,1	>200	<0,2	650-900	75	12	13

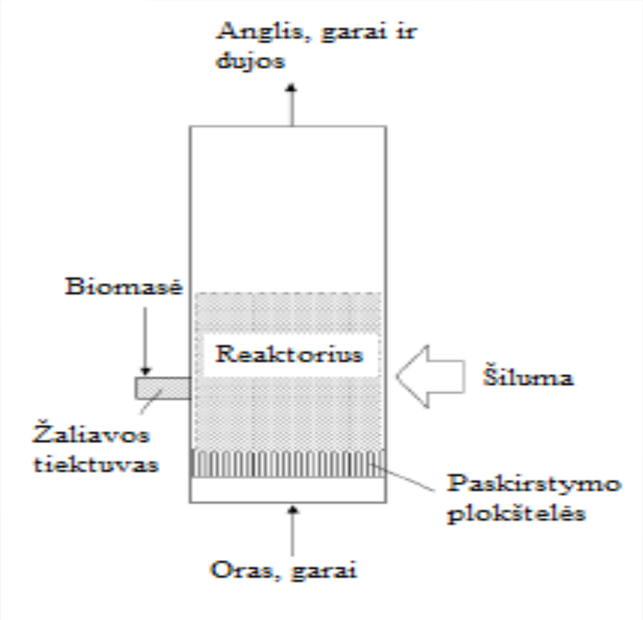
Effect of pyrolysis parameters on the product distribution

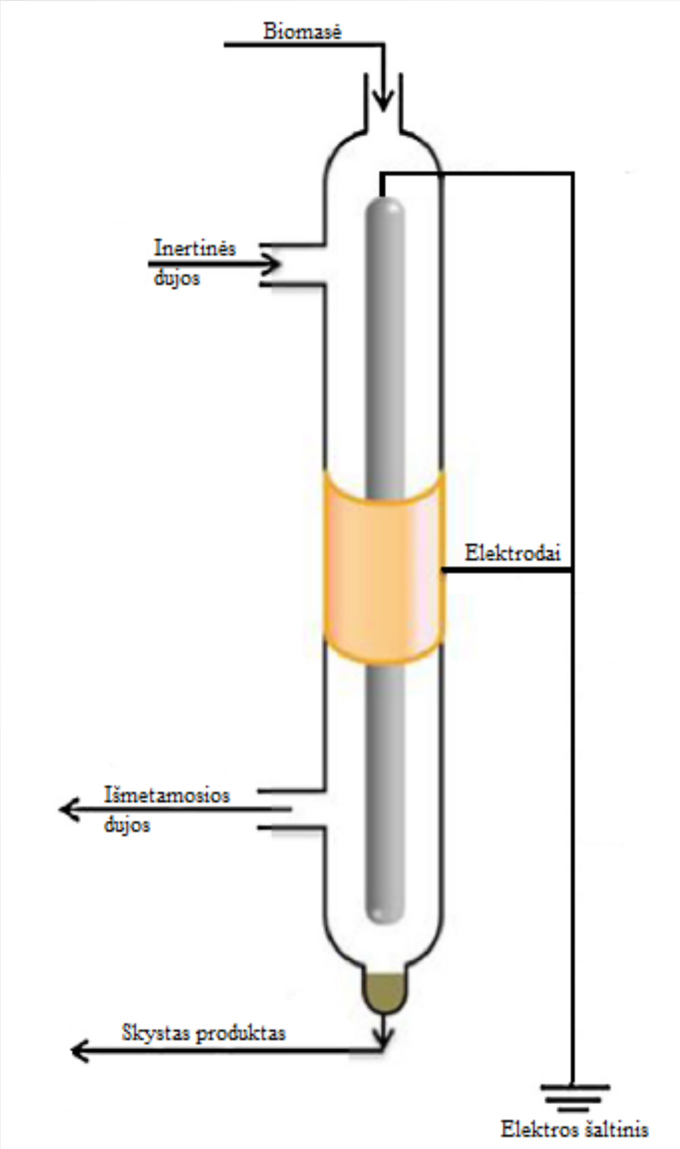
- Effect of pyrolysis temperature ;
- Effect of particle size ;
- Pressure;
- Residence time ;
- Feedstock characterization
- Type of reactors.

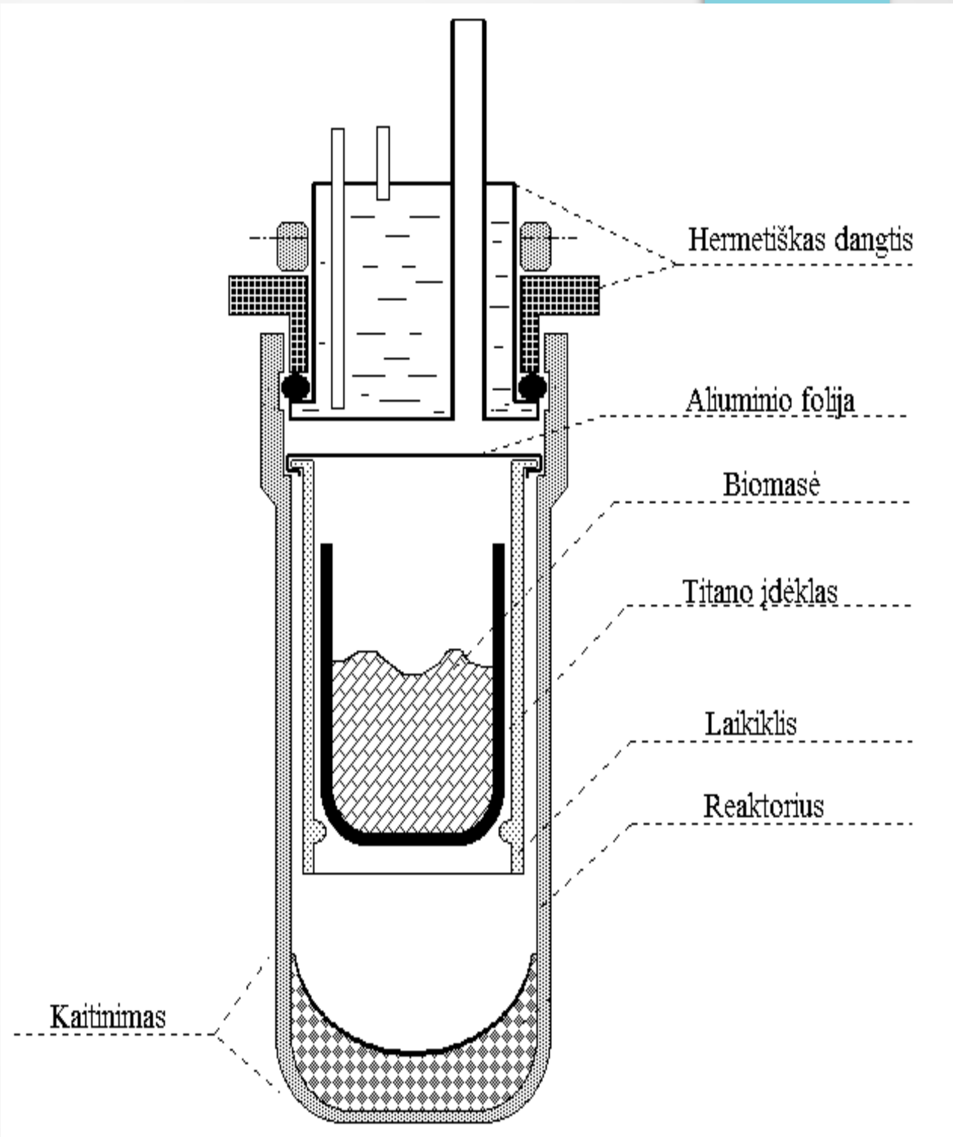
TYPE OF REACTORS.

Batch Process;
Fixed bed and fluidized bed reactors






Biomasė
Inertinės dujos
Elektrodai
Išmetamosios dujos
Skystas produktas
Elektros šaltinis


Hermetiškas dangtis
Aliuminio folija
Biomasė
Titano įdėklas
Laikiklis
Reaktorius
Kaitinimas

The main aim of work: To investigate the possibilities to produce bio-oil from macro-algae .

Objectives:

To examine the possibilities to increase the yield of pyrolysis oil by using different raw material mixtures like macro-algae and HDPE plastic waste in the batch reactor.

To analyze the possibilities to separate the hydrocarbon fraction from pyrolysis bio-oil in the distillation unit under vacuum pressure.

To determine the properties of hydrocarbon mixture like viscosity, density, ash content and elemental composition.

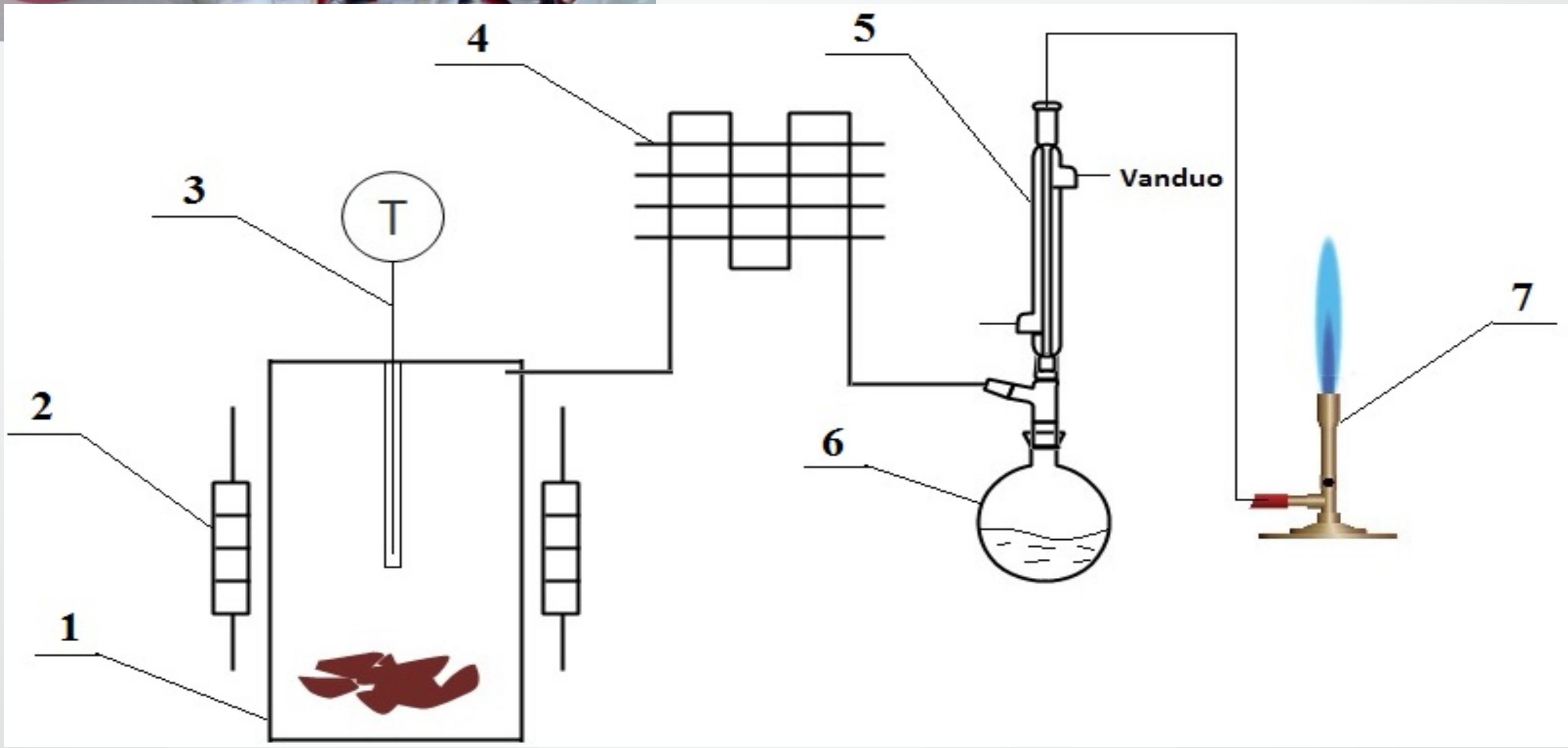
To identify the individual hydrocarbons and its amount by using gas chromatography.

Pyrolysis was done by two stages:
the first stage was pure macro-algae;
second phase of the pyrolysis process as a raw material was used macro-algae and HDPE plastic waste.
Both pyrolysis processes is carried out at three different temperatures 300, 350, 400^{o}C.

70 % macroalgae and 30 % HDPE plastic
50 % macroalgae and 50 % HDPE plastic
30 % macroalgae and 70 % HDPE plastic

MACRO-ALGAE *Cladophora*

Polyethylene (HDPE):



PRODUCT YIELDS FROM MACRO-ALGAE

Pyrolysis Temperature °C	**Liquid yields, %**	**Solid yield, %**	**Gas, %**
300	33.40	46.53	20.07
350	34.54	44.78	20.68
400	34.52	41.85	23.63

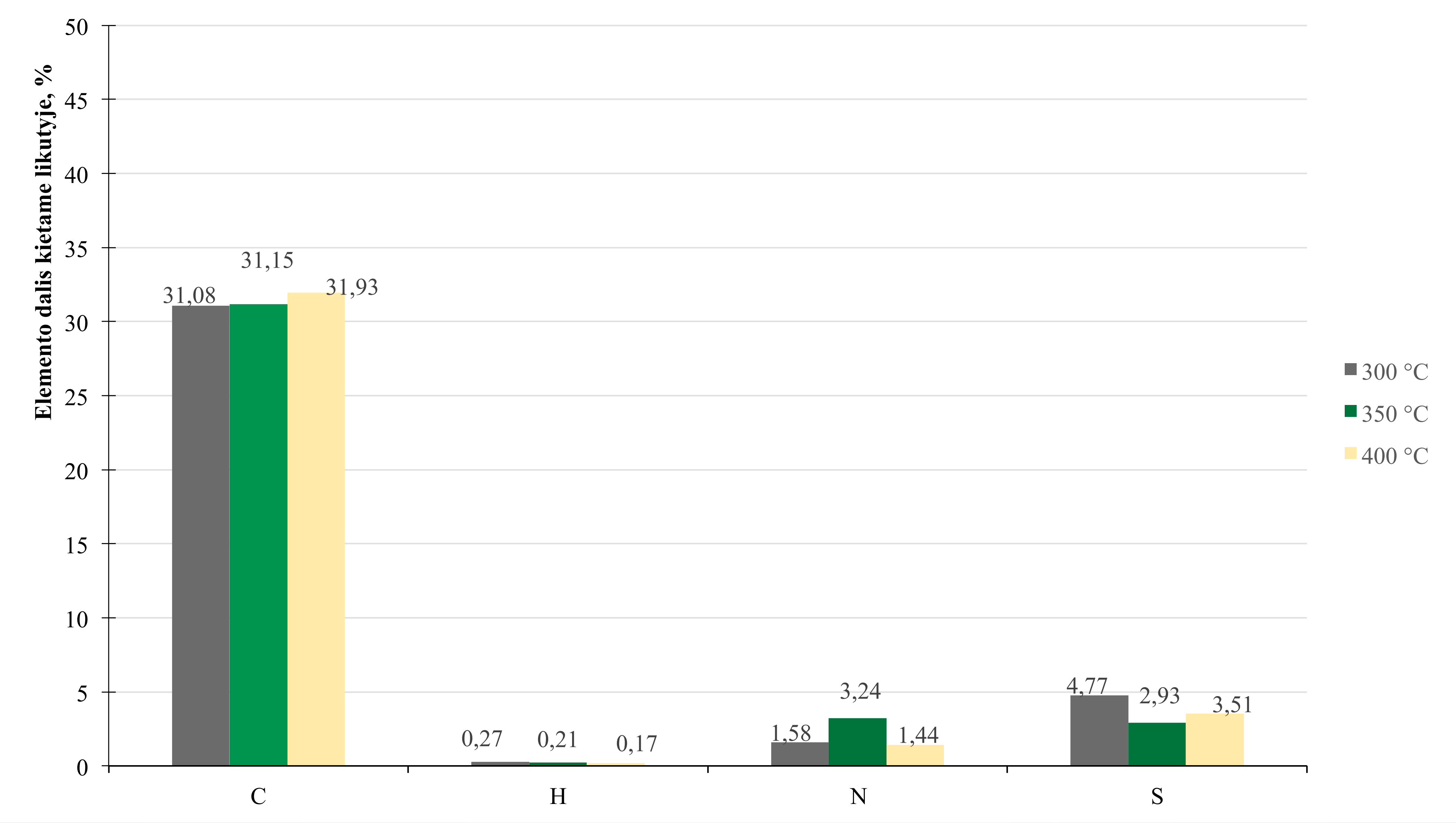
The pyrolysis process at 50:50 ratios of raw material

Pyrolysis temperature, °C	Liquid, %	Solid, %	Gas, %
300	28,86	59,17	11,97
350	36,05	36,46	27,49
400	45,53	25,63	28,84

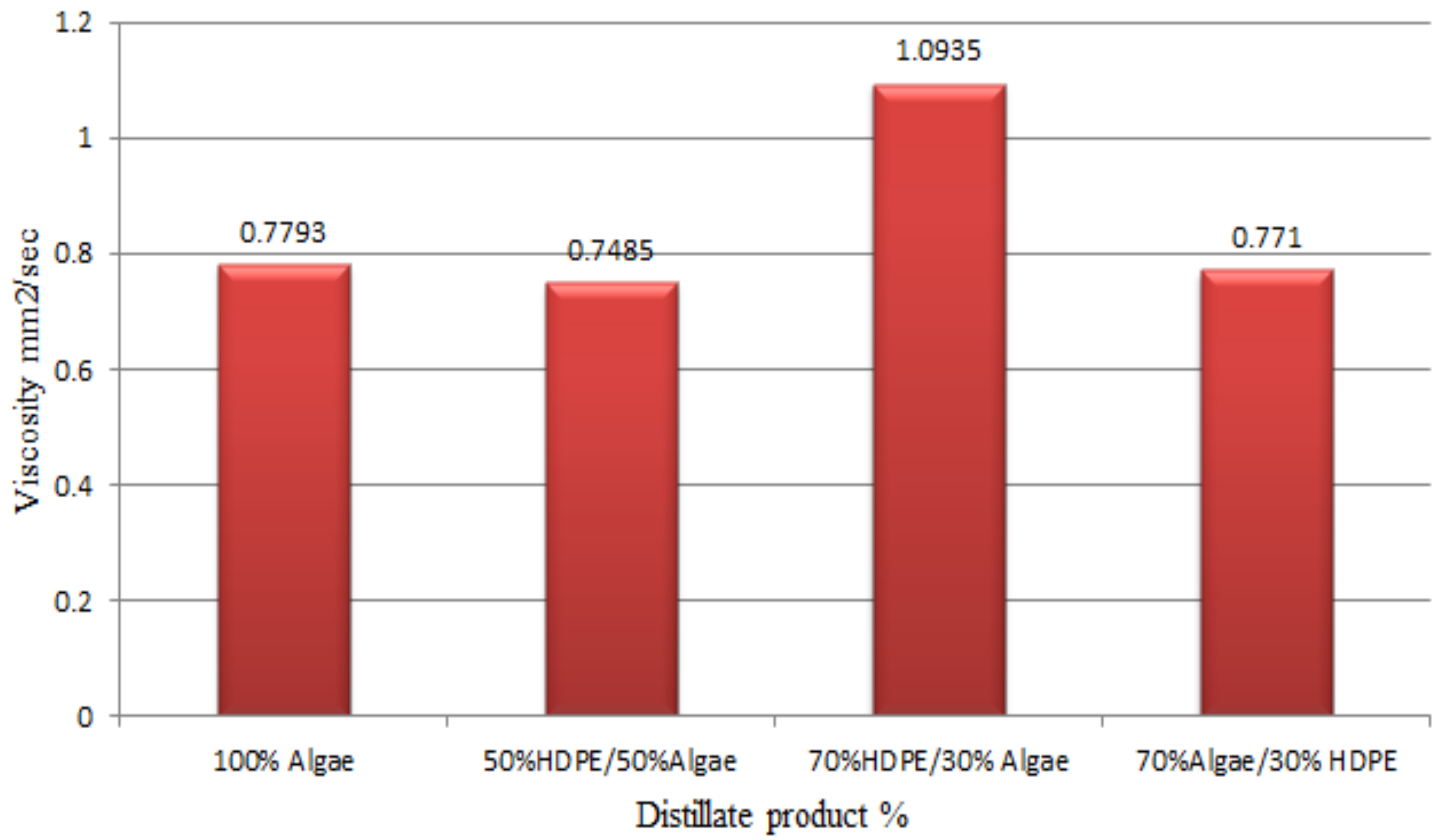
PYROLYSIS PROCESS AT 400^{O}C

Sample Mixtures	Liquid (%)	Solid Form (%)	Gas (%)
100% Algae	35.12	42.38	22.50
50% Algae & 50% HDPE	47.84	32.82	19.34
70% HDPE & 30% Algae	**61.12**	18.18	20.70
70% Algae & 30% HDPE	38.64	36.88	24.48

THE ELEMENTAL COMPOSITION OF THE SOLID RESIDUE FROM MACROALGAE BIOMASS

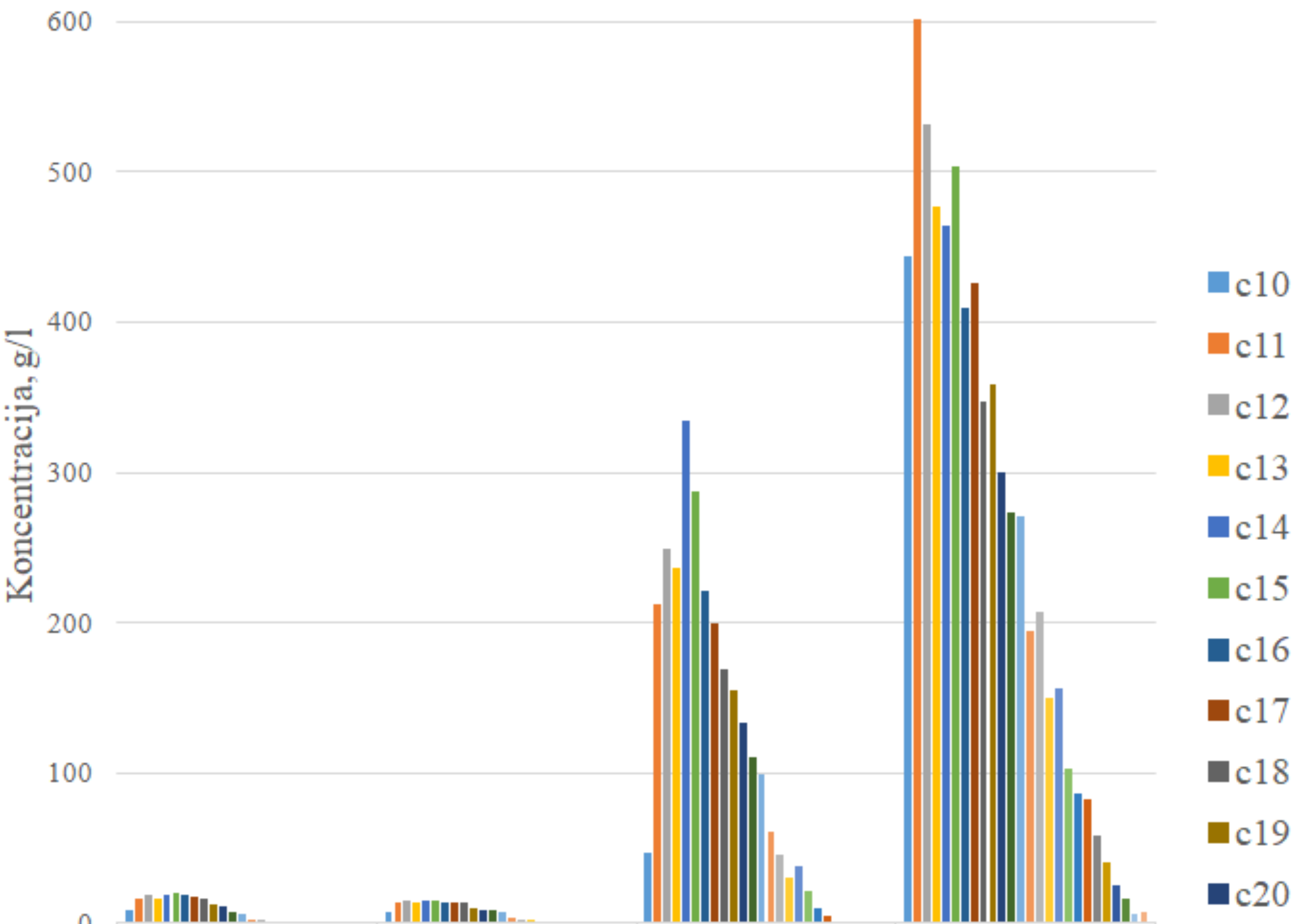


Analysis of Viscosity

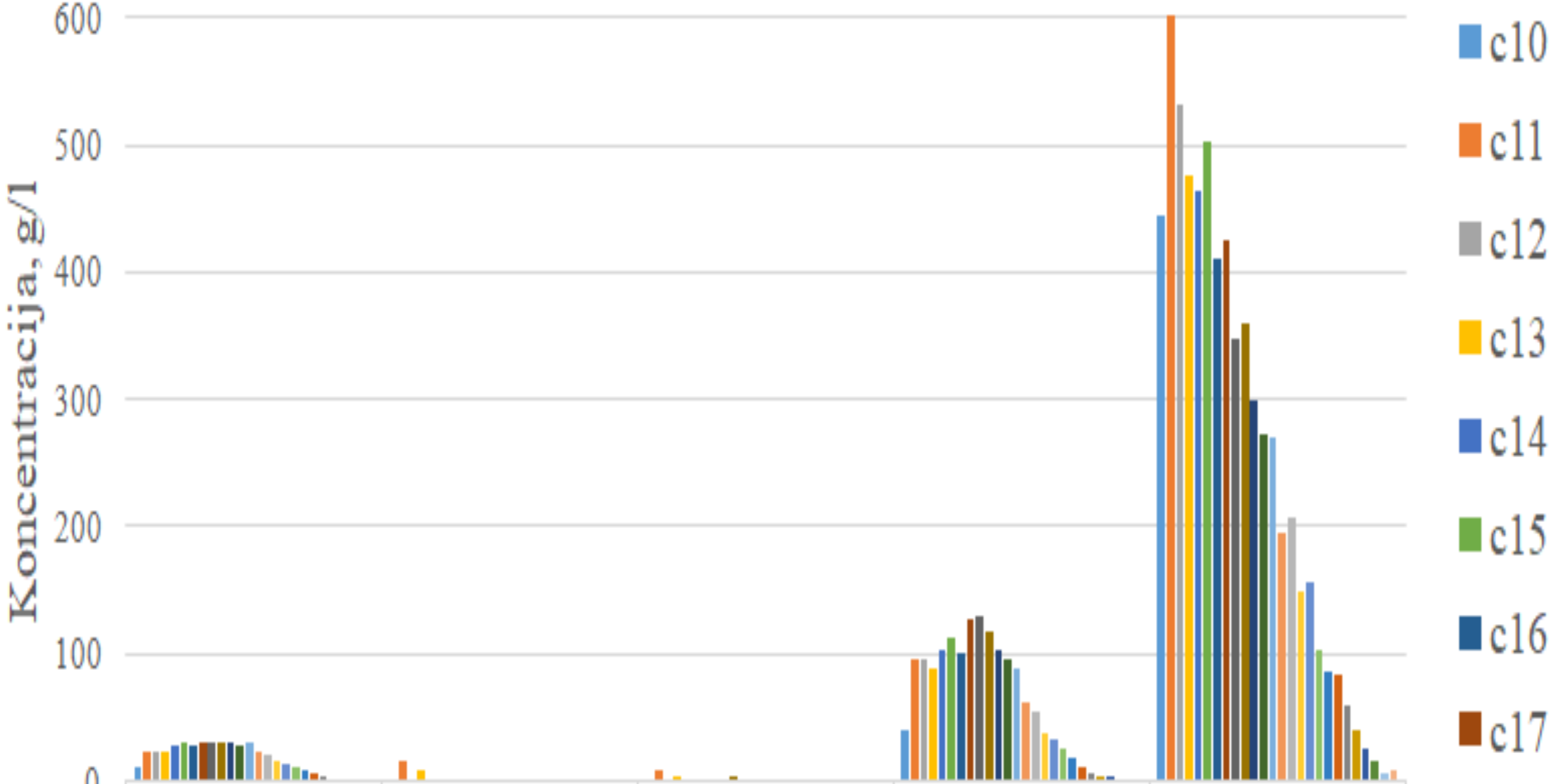


ELEMENTAR ANALYSIS

Samples	Nitrogen %	Carbon %	Sulfur %	Hydrogen %
100%	0.061	2.616	0.485	7.140
50%HDPE/ 50%Algae	0.315	4.242	0.239	8.255
70%HDPE/ 30%Algae	0.341	4.181	0.215	7.605
70%Algae/ 30%HDPE	0.204	2.191	0.211	6.769

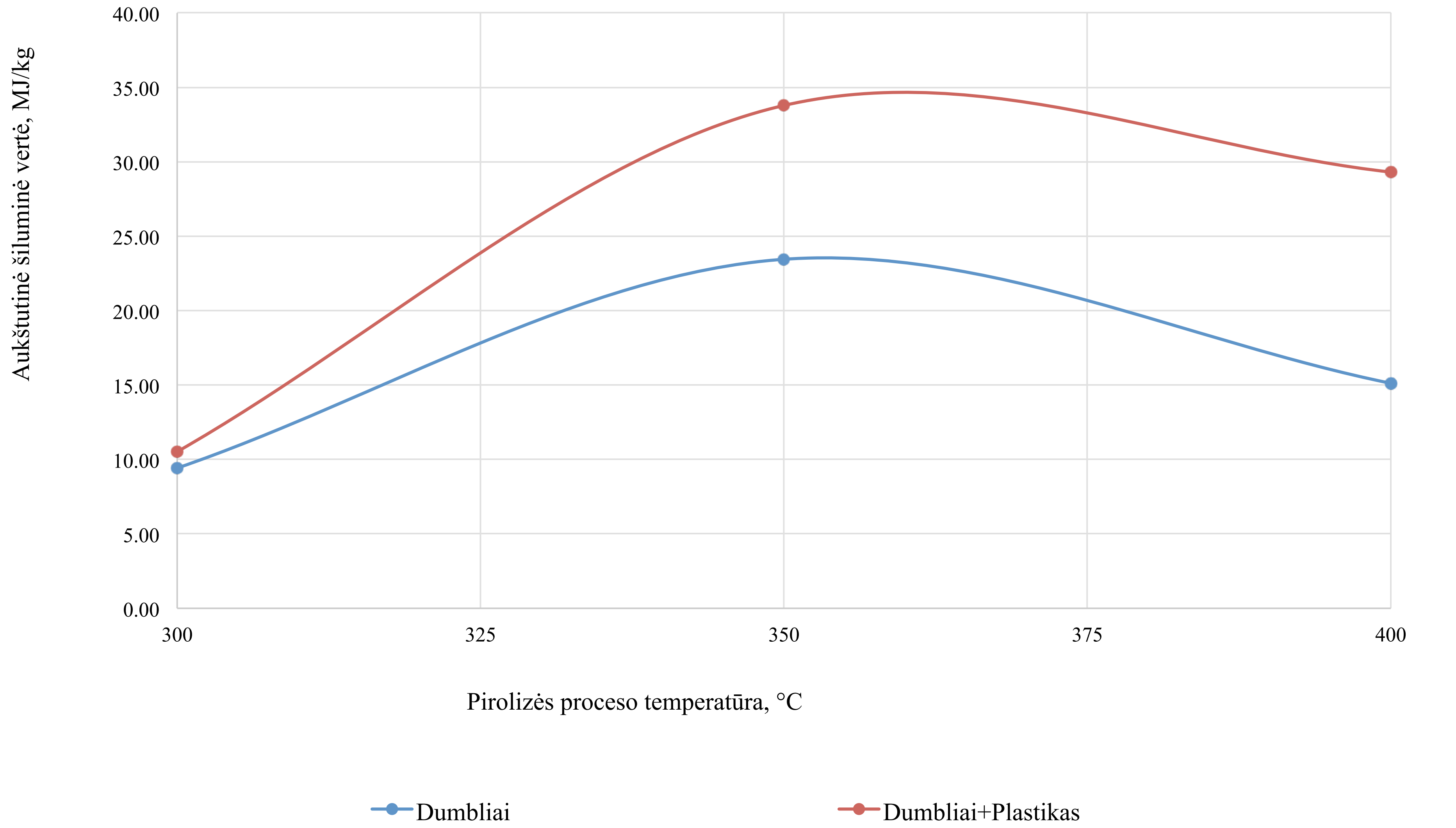


	300 °C mišinys	350 °C mišinys	400 °C mišinys	Nafta
c10	8,3375	7,2185	47,2305	444,4
c11	17,0675	13,5495	212,646	601,92
c12	18,611	15,368	249,0765	531,68
c13	16,6825	13,5965	236,354	476,64



	100 % dumblių	70 % dumblių/30 % HDPE	50 % dumblių/50 % HDPE	30 % dumblių/70 % HDPE	Nafta
c10	10,524	2,245	2,031	40,071	444,4
c11	23,5725	16,118	7,408	95,7365	601,92
c12	24,1815	0	0	95,5465	531,68
c13	23,793	7,323	2,4665	88,959	476,64
c14	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

CALORIFIC VALUE



CONCLUSIONS

In this research algae and algae mixture with waste plastic used as raw material in slow pyrolysis process. Pyrolysis process was held at 400^{o}C with different proportions of raw material used. After collection of liquid product from pyrolysis process, distillation can be done in that liquid product. The distillated bio-oil was conducted several property test like density, viscosity, ash test, gas chromatography and elemental analysis.

Results showed that by adding waste plastic in algae, pyrolysis process the liquid product yield is increase and also distillated bio-oil from waste plastic and algae gives better property test. Best liquid product properties obtained from 400^{o}C temperature.

Experimental Research of pyrolysis products from waste plastics as gasoline blends.

The main aim of work: To investigate production of gasoline fraction from waste HDPE by pyrolysis and to study the properties of mixtures with pyrolysis gasoline.

Objectives:

Perform pyrolysis of high density polyethylene (HDPE) waste and identify products. Spectral methods assign chemical structure of pyrolysis oil.

Separate gasoline fraction from pyrolysis oil. Explore gasoline fraction, chemical composition by Gas Chromatography, physical and chemical properties by BS EN228:2013 standard.

To investigate the gasoline fraction influence on 92 brand and manufacturing gasoline's mixtures distillation characteristics, density, viscosity..

METHODOLOGY

This work investigated the pyro-gasoline from the HDPE by the process of pyrolysis. The pyrolysis process of HDPE plastic waste was carried out at **332.8 - 441°**C temperature. The results indicate that is forming 3.75% of gases, 95.63% of pyrolysis oil and only 0.61 % of the solid residues.

METHODOLOGY

Sampl es no	Pyrolysis gasoline	Gasoline from ORLEN LIETUVA	Gasoline from STATOIL
1	100%	0	0
2	5%	95%	0
3	5%	0	95%

ANALYSIS

- Distiliations characteristics;
- Density test;
- Viscosity;
- Ash test;
- Spectral analysis;
- Gas Chromatography analysis;
- Driveability Index;
- The lowest ambient temperature.

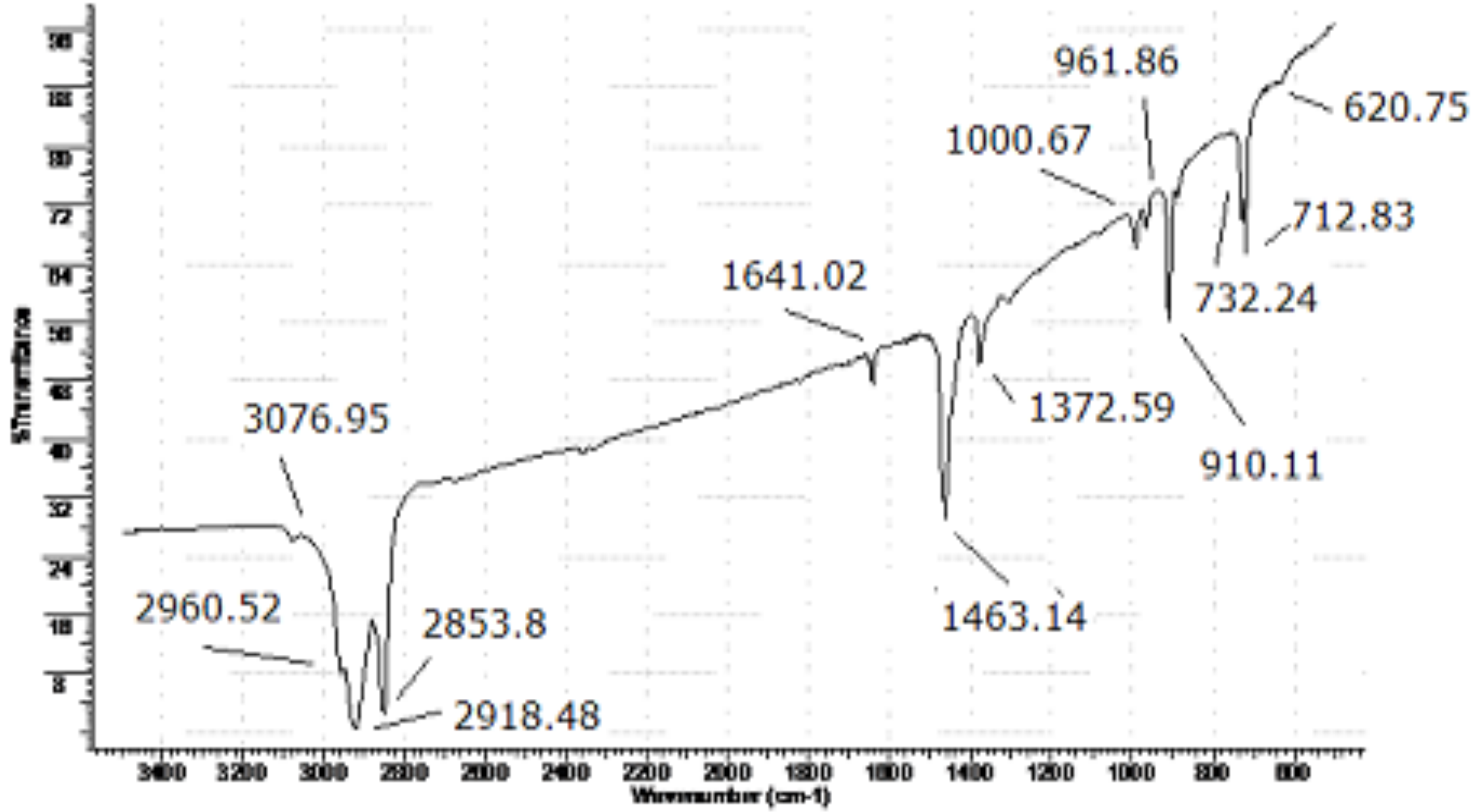
Pyrolysis products

Products	HDPE	
	mass (g)	Percent age (%)
Total sample(HDPE)	1296.56	100
Pyrolysis oil	1239.96	95.63
Char(residue)	7.98	0.61
Gas(flare)	48.62	3.75

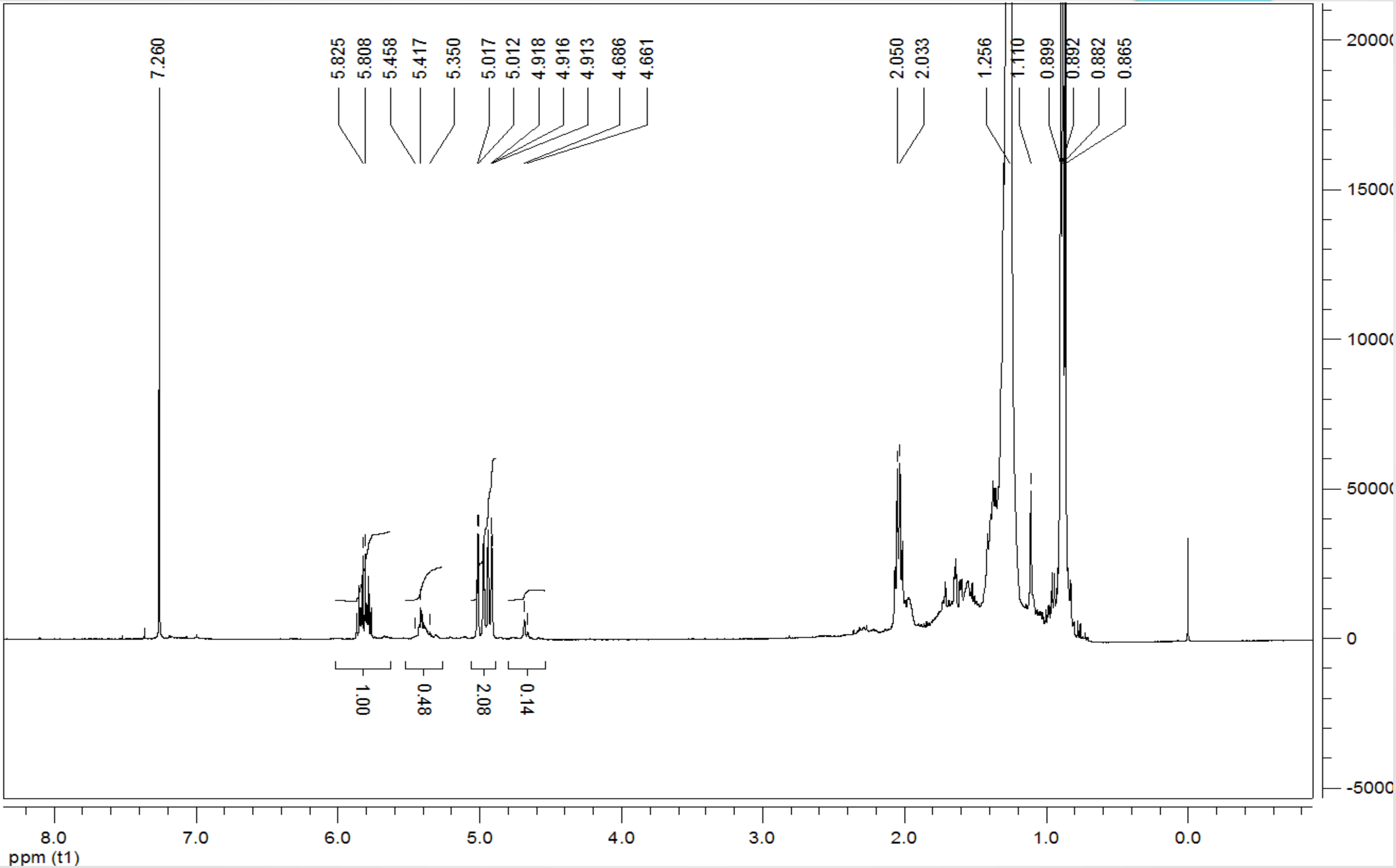
PYROLYSIS OIL PHYSICAL AND CHEMICAL PROPERTIES

Density, g/cm³	**0,8250**
Viscosity, mm²/s	**5,1705**
Pour point, ºC	**35**
Filtering temperature, ºC	**20**
Calorific value,KJ/kg	**45,993**
The oxidative stability, min	**32,45**
The ash content	**0,0005**

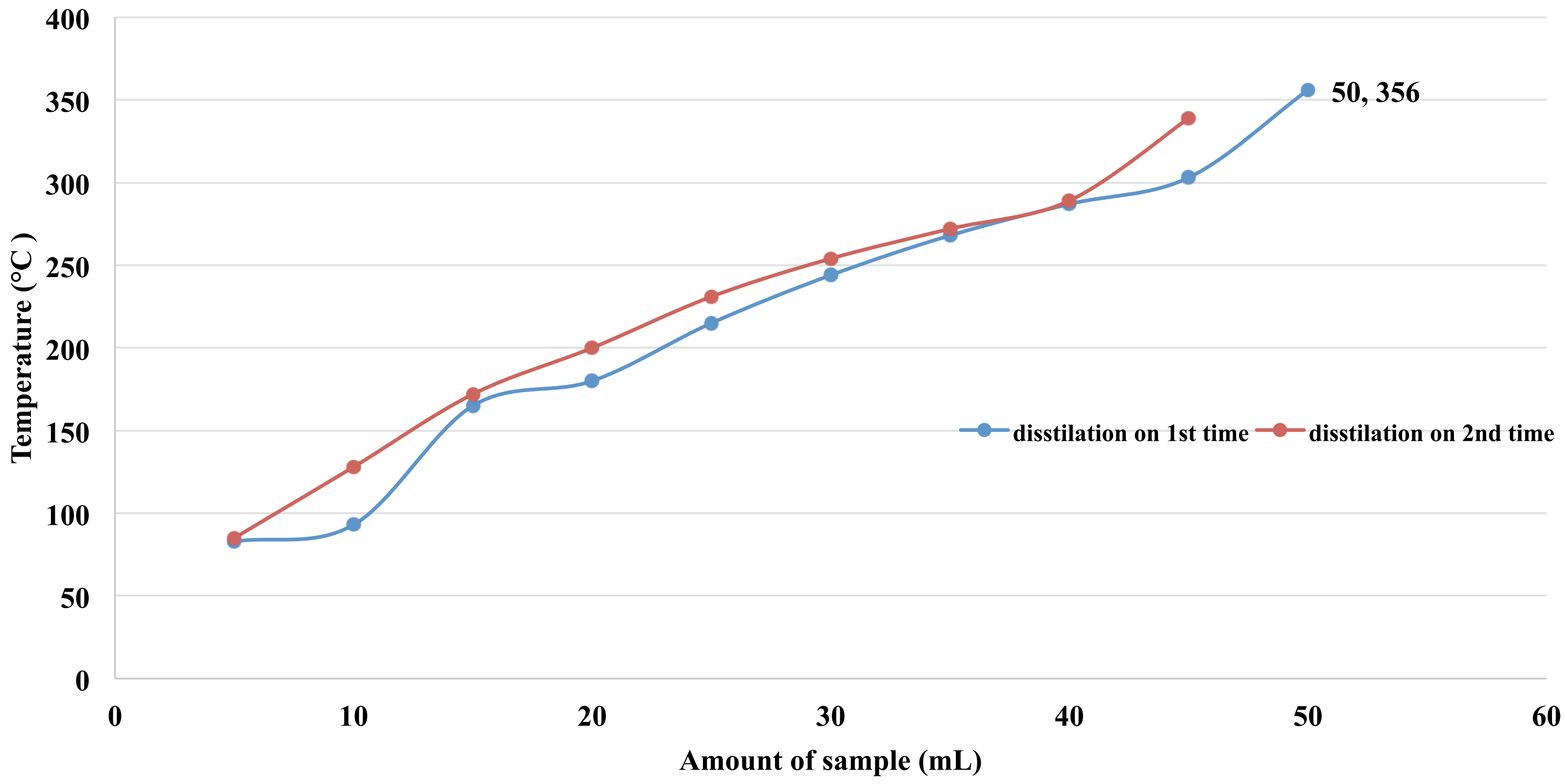
SPECTRAL ANALYSIS IR spectrum



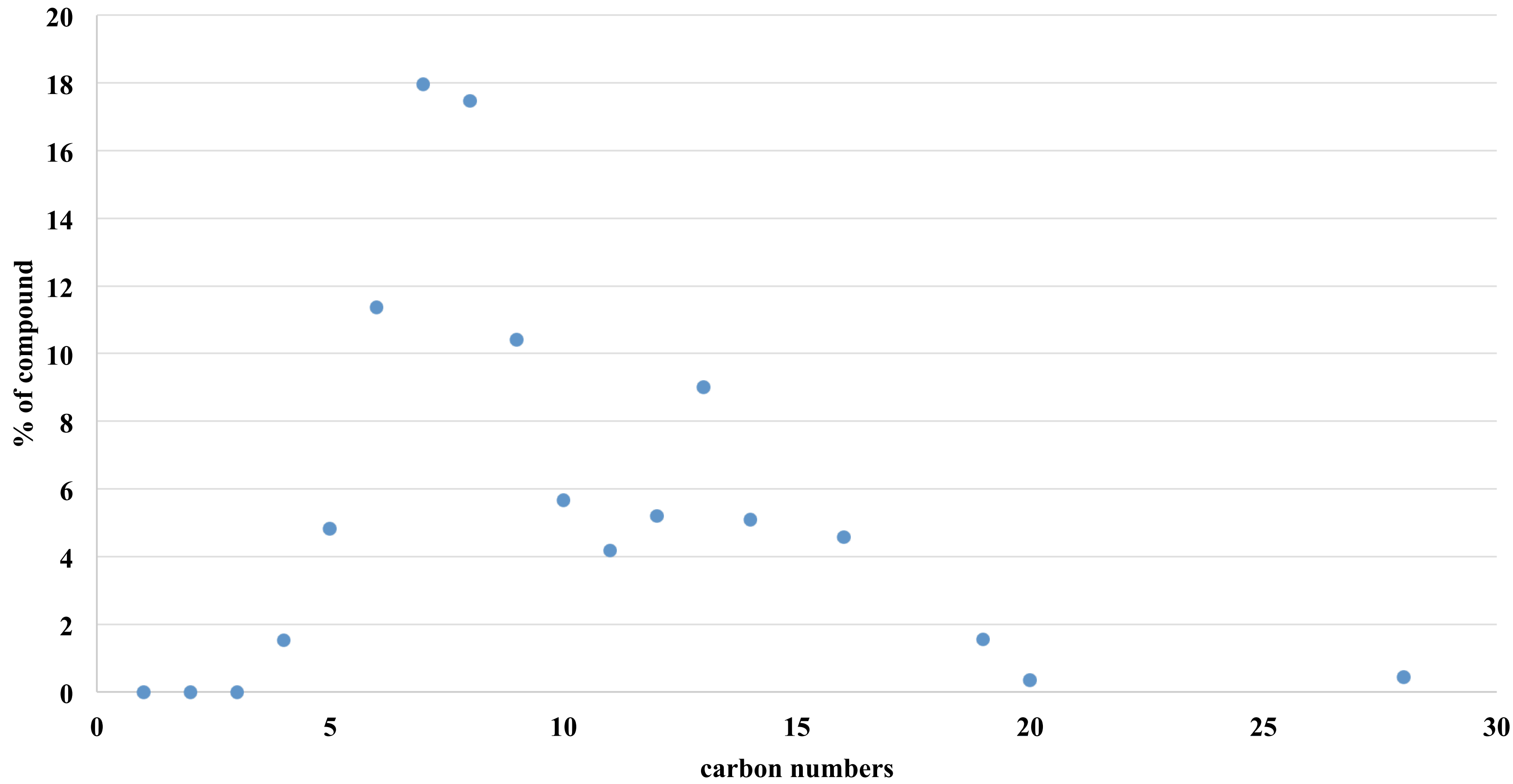
SPECTRAL ANALYSIS ^{1}H-*NMR* spectrum



Pyrolysis oil distiliation

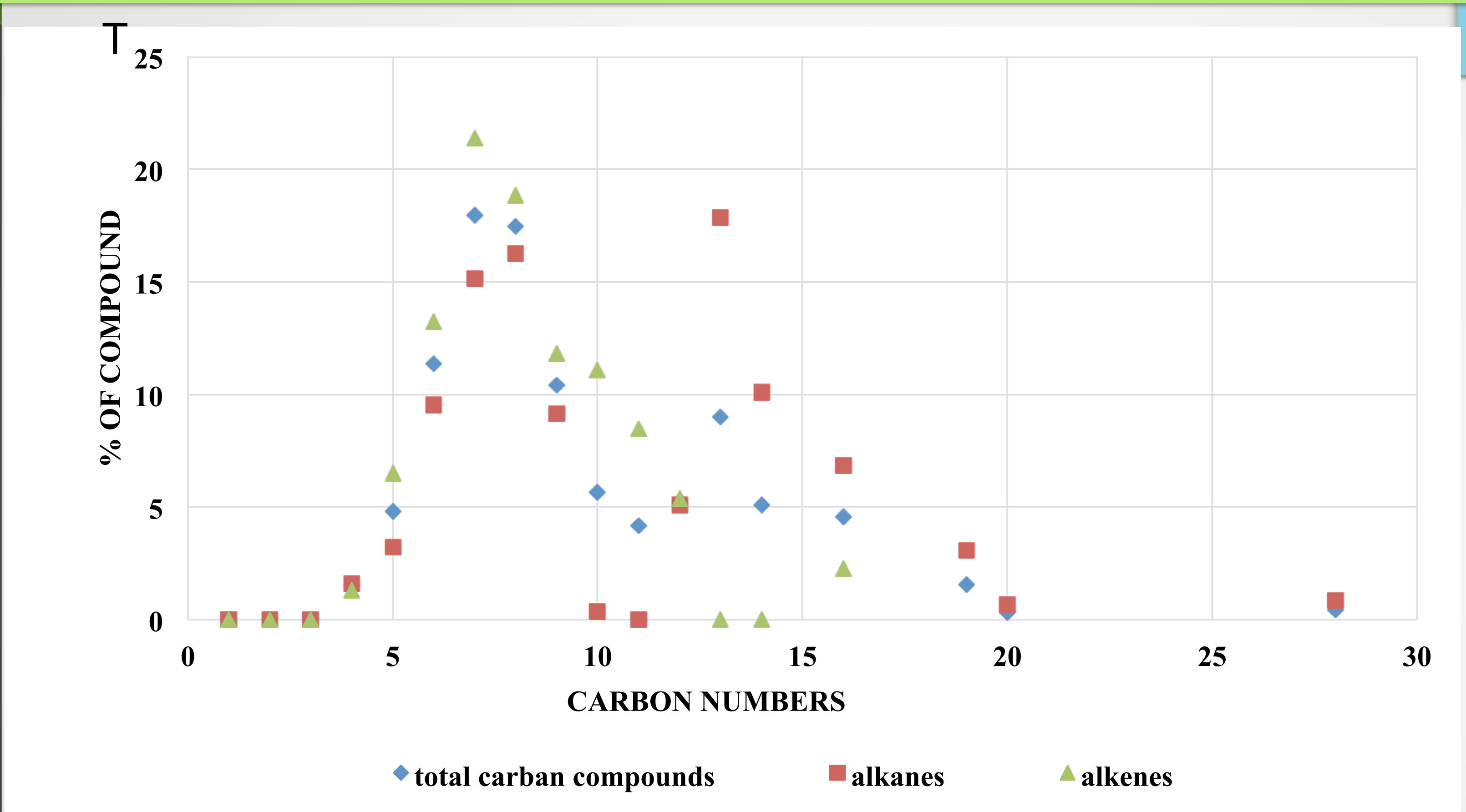


GAS CHROMATOGRAPHY



THE HYDROCARBONS HAVING ABOVE 1% FROM THE TOTAL WEIGHT OF MIXTURE.

S.no		Name of Carbon compound	Peak area, %
1	C_5H_{10}	Pentene-1	1.74
2	C_5H_{12}	Pentane	1.62
3	C_6H_{12}	2-Methylpentene-1	4.16
4	C_6H_{14}	3-methylpentane	2.93
5	C_6H_{12}	Cyclohexane	1.22
6	C_8H_{14}	1-methylethenylcyclopentan	1.53

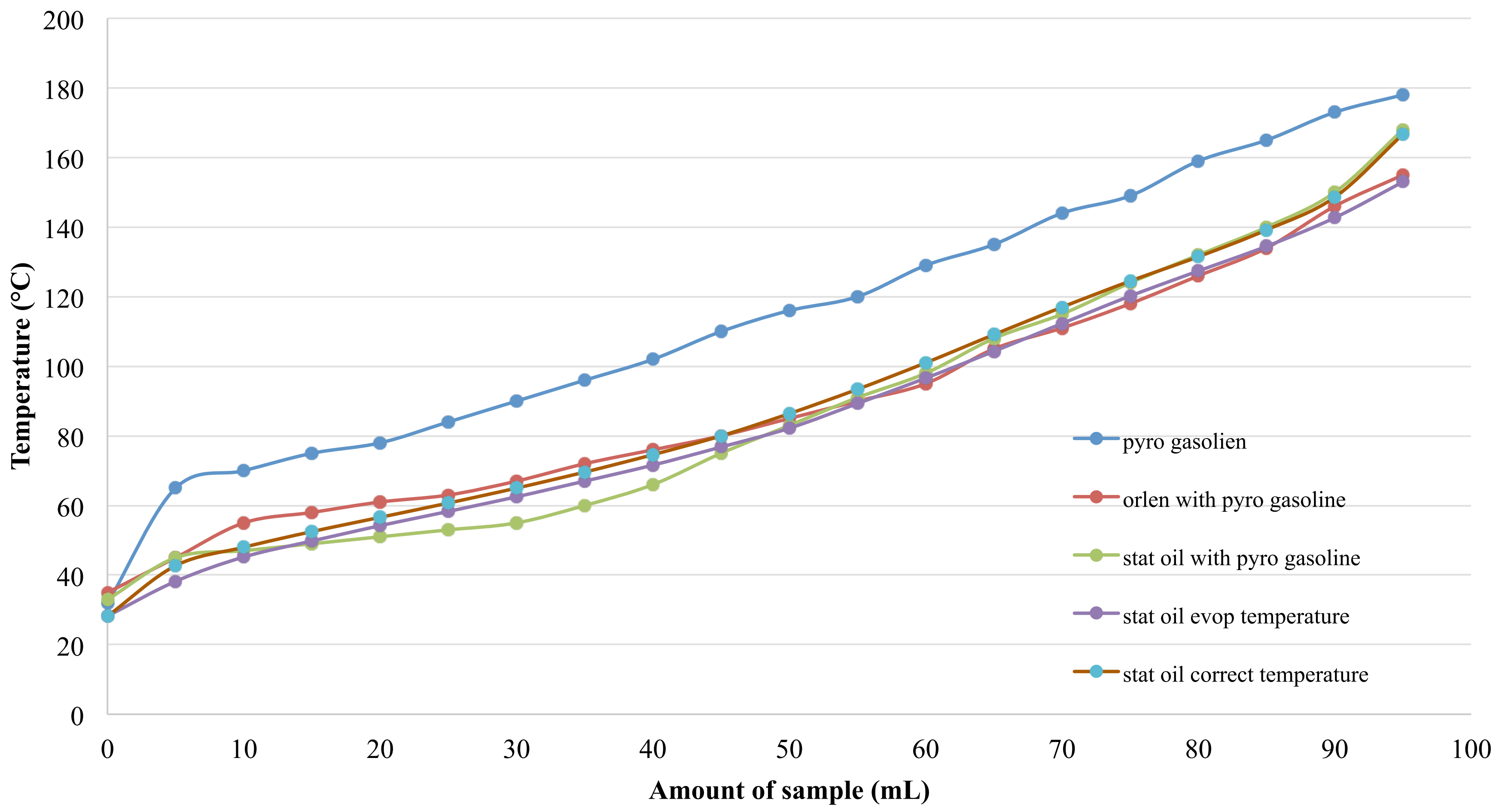


The percentage distribution of carbon compounds, alkanes and alkenes of the gasoline fraction, by carbon number.

PYRO-GASOLINE MIXTURES WITH GASOLINES

Mixtures	Pyro-gasoline 5% + ORLEN gasoline 95%	Pyro-gasoline 5% + STATOIL gasoline	Only STATOIL
Density, g/cm³	0.7352	0.7387	0.7372
Viscosity, m²/s	0.4826	0.4839	0.4725
The ash content, %	0.29	0.27	0.16

DISTILLATION



C

1. It was determined that the pyrolysis process of the HDPE plastic waste carried out at 332.8°C - 441°C temperature is forming 3.75% of gases, 95.63% of pyrolysis oil and only 0.61 % of the solid residues. The pure pyrolysis oil due to its high viscosity, high pour point temperature and filtration, it is not possible use as a motor fuel.
2. Chemical structure of pyrolysis oil was investigated by spectral methods, IR spectrum showed no heteroatom compounds in pyrolysis oil, only hydrocarbons were obtained. ^{1}H NMR spectrum has no signals which can be attributed to aromatic protons.
3. The distillation of pyrolysis oil had been carried out. Its light fraction accounted for 37.28%, and have 14.87% pyro-gasoline and 22.41% pyro-diesel mass by volume.

4. Over than 80 hydrocarbons were identified in pyro-gasoline by gas chromatography. It has been estimated, that the content of alkanes and alkenes is almost equal quantities 51:49 % by volume.

5. The experimental results showed that mixtures of 5 % pyro-gasoline and 95 % basic ORLEN or commercial STATOIL gasoline by volume, according to all parameters it has been acceptable of BS EN 228: 2013 standard. The research of pyrolysis products from HDPE waste plastics as gasoline blends, showed that the mixtures of small quantities pyro-gasoline possible to use as a motor fuel.

6. The results obtained from this study show usefulness and feasibility of pyrolysis process of HDPE plastic as an alternative approach to feedstock recycling.

Thank You! Any Questions?