Dmitry Mendeleev University of Chemical Technology of Russia
Department of Technology of Basic Organic and Petrochemical Synthesis

Wacker-type oxidation of fatty acids and derivatives

Authors:
Svetlana I. Gustyakova
Valentin N. Sapunov
Mikhail S. Voronov
Ilona S. Kozeeva

About Waker-type process

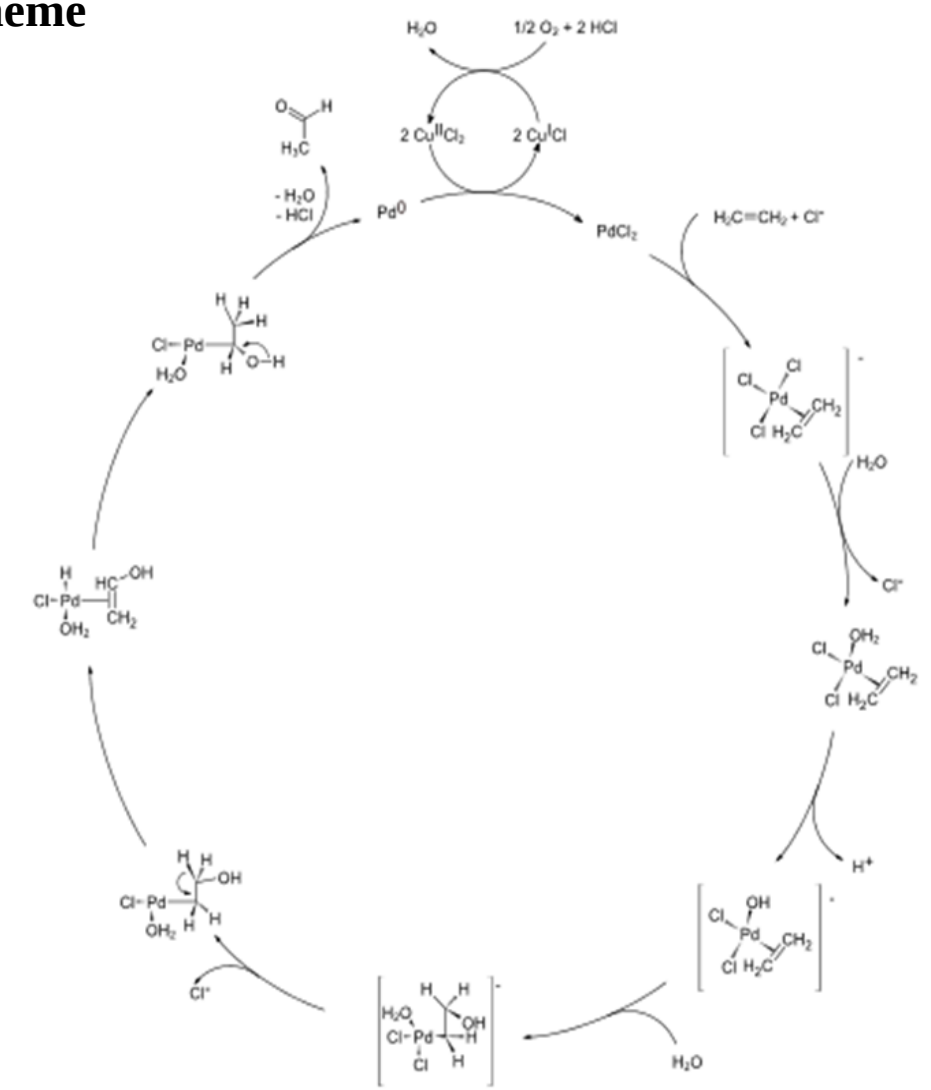
Description the process

The Wacker process is a process developed and introduced in the 1960s by Waker-Chemie and Farbwerke Hoechst for the production of acetaldehyde by the direct oxidation of ethylene.

Conditions

Parameters	Value
pH	0-2
$PdCl_2$	0,3 – 0,5 mass.%
$CuCl_2$	10,0-25,0 mass.%
Temperature	50-70°C
Pressure	10 atm

Catalytic scheme



Introduction

Objective

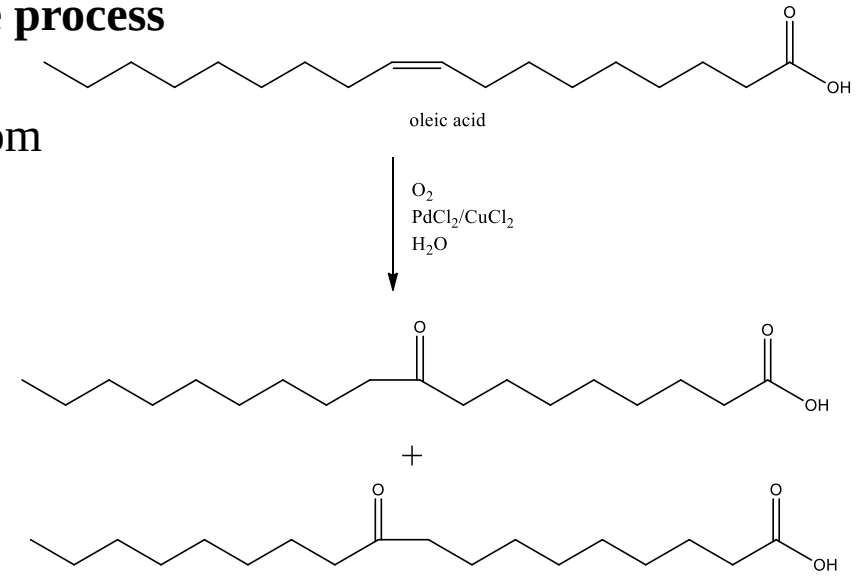
Functionalization of double bonds of fatty acids and their derivatives into fatty ketones using industrial approaches Waker-type process.

Application

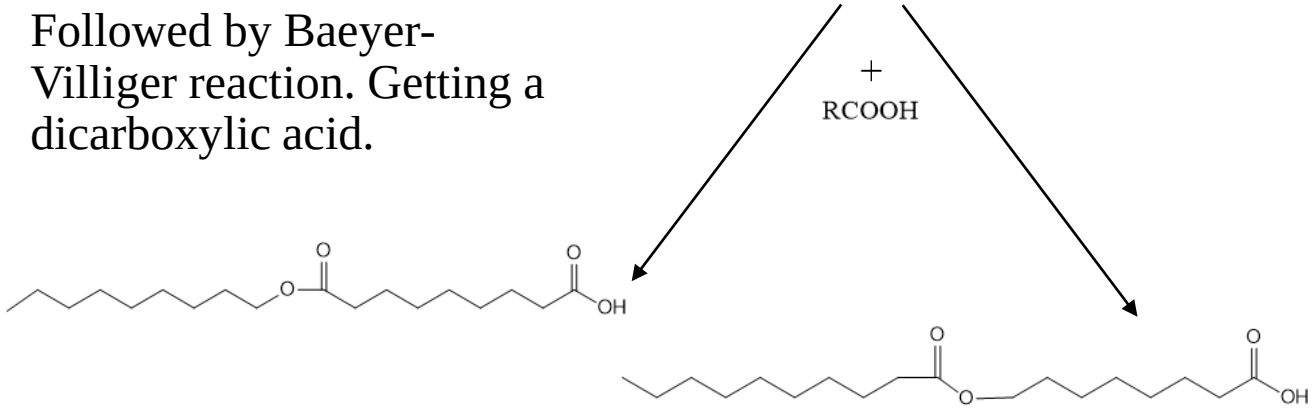
We are going to oxidize fatty ketones to dicarboxylic acids, which can be used as, for example, plasticizers and as raw materials for the production of polyester fibers.

General scheme of the process

Obtain fatty ketones from vegetable oils and their derivatives (Wacker process).

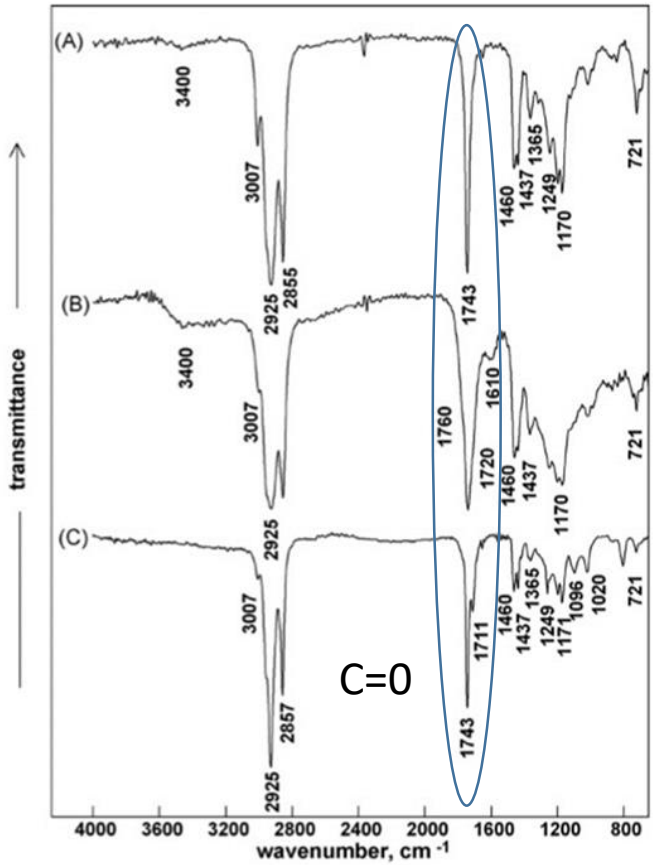


Followed by Baeyer-Villiger reaction. Getting a dicarboxylic acid.



Background

Description in literature



FT-IR spectra of rapeseed oil methyl ester (A), liquid (B) and volatire (C) oxidation products

Analytics using in the research

Spectrometric analysis methods

- ✓ Fourier transform infrared spectroscopy (FTIR)
- ✓ NMR ^{1}H spectroscopy
- ✓ NMR ^{13}C spectroscopy ЯМР

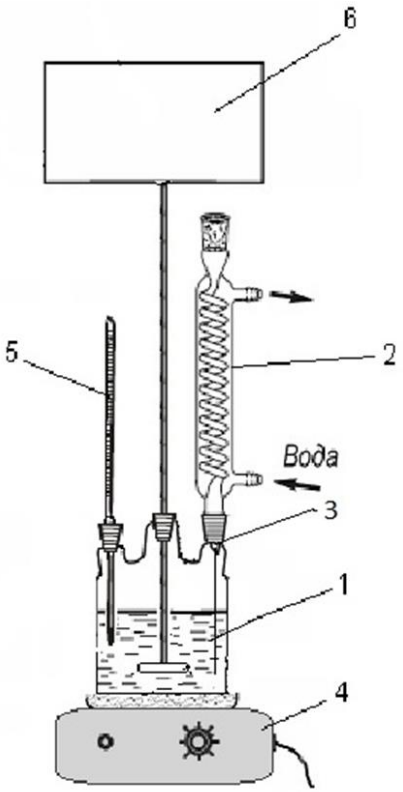
Titrimetric methods of analysis

- ✓ Carbonyl number

Synthesis in a flask (air bubbling)

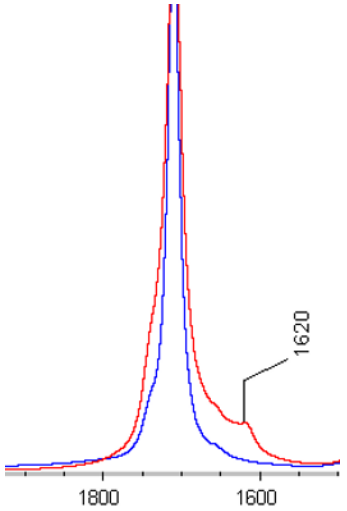
Installation Description

Parameters	Value
pH	0-2
$PdCl_2$	0,3 – 0,5 mass.%
$CuCl_2$	10,0-25,0 mass.%
Temperature	50-70°C
Air flow rate	0,002 m^3 per min



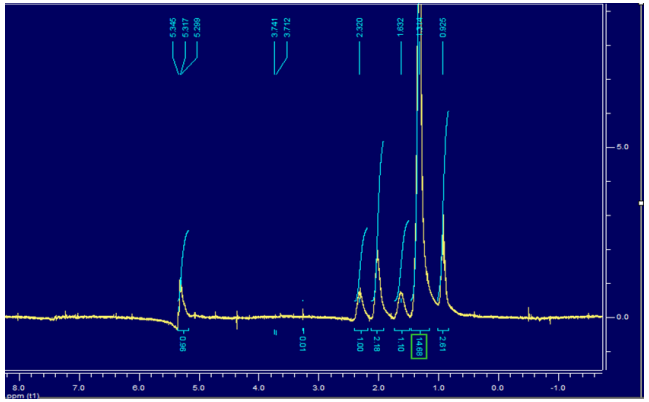
Laboratory setup for carrying out Waker type process:1 - glass reactor without a jacket, 2 - reflux condenser, 3 - bubbler, 4 - magnetic stirrer with heating, 5 - thermometer, 6 - overhead stirrer.

Analysis of the product

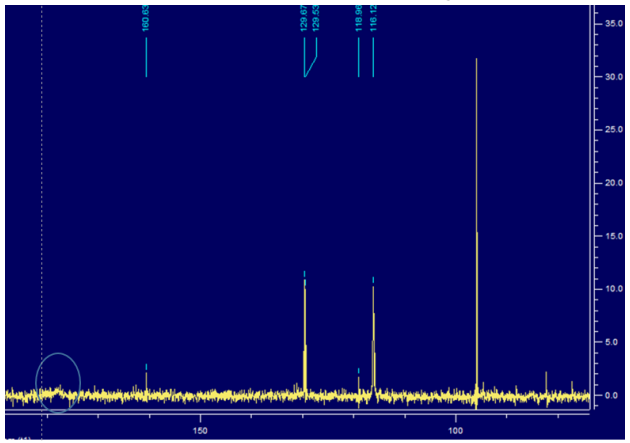


Fragment of the IR spectrum

Blue line - raw materials
Red line - product



NMR ^{1}H. Conversion by // 5-6%



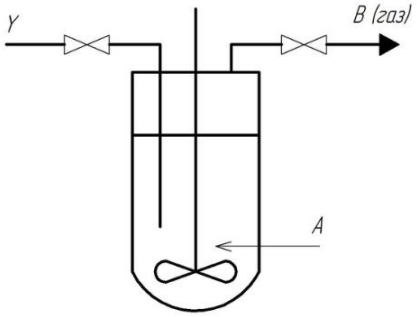
NMR ^{13}C. The absence of a carbonyl peak (at 210 ppm)

Conclusion

The reaction did not work under the specified conditions.

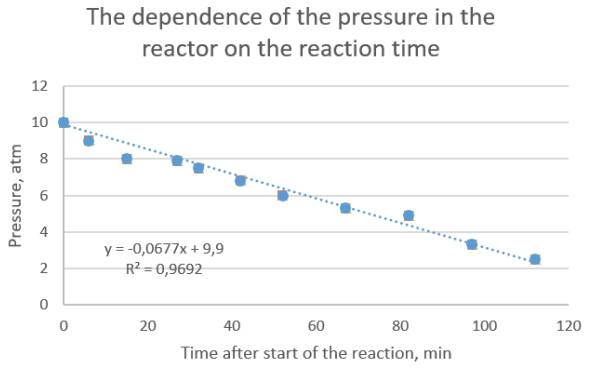
Synthesis batch reactor

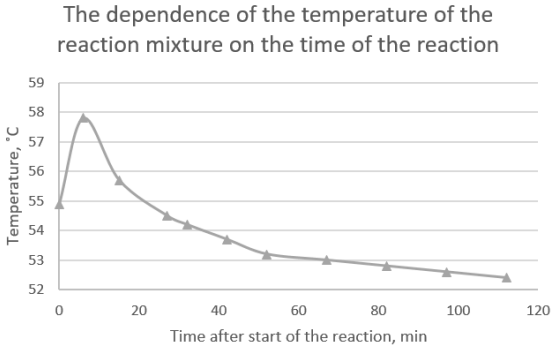
Installation Description



Parameters	Value
pH	0-2
$PdCl_2$	0,3 – 0,5 mass.%
$CuCl_2$	10,0-25,0 mass.%
Temperature	50-70°C
O_2 pressure	10 atm

Kinetics

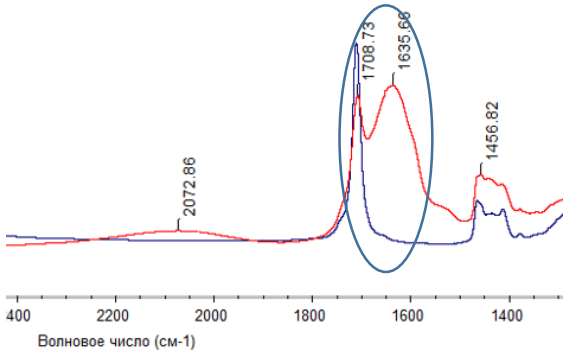




Conclusions

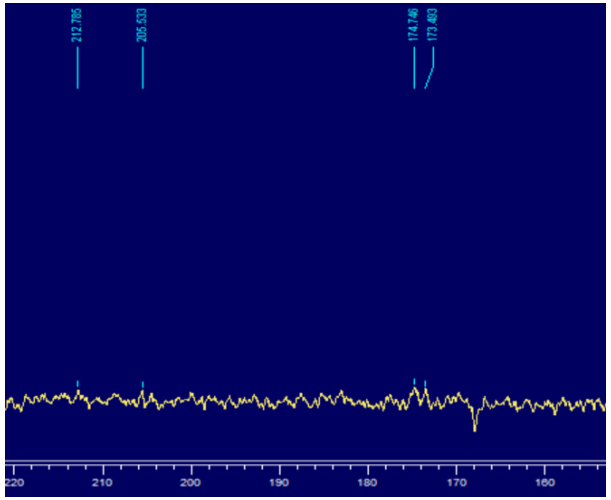
- The reaction takes place under pressure
- Zero order of reaction with respect to oxygen

Analysis of the product



Fragment of the IR spectrum

Blue line - raw material
Red line - product

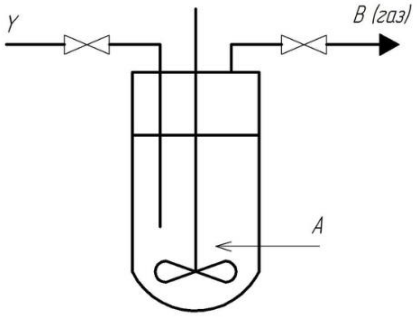


Fragment of the NMR ^{13}C

Presence of a carbonyl peak – 170 ppm –oleic acid, 210 ppm fatty ketones

Synthesis batch reactor

Installation Description

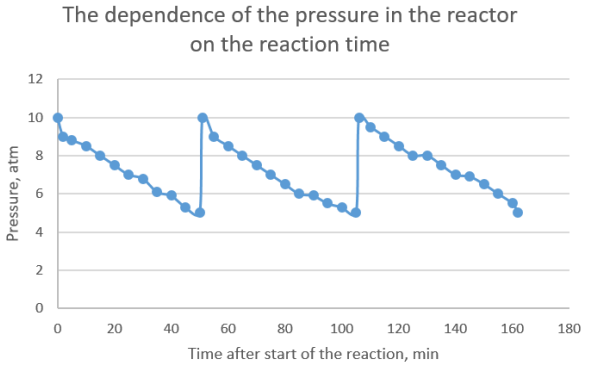


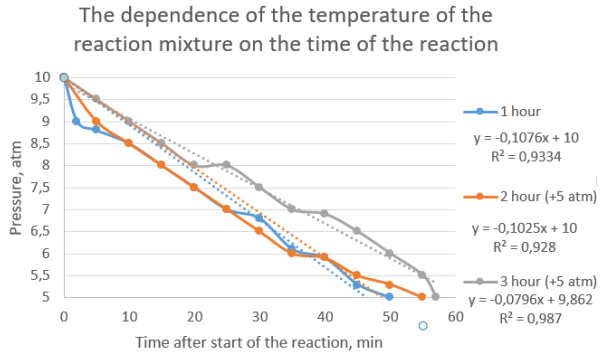
Parameters	Value
pH	0-2
$PdCl_2$	0,3 – 0,5 mass.%
$CuCl_2$	10,0-25,0 mass.%
Temperature	50-70°C
O_2 pressure	10 atm

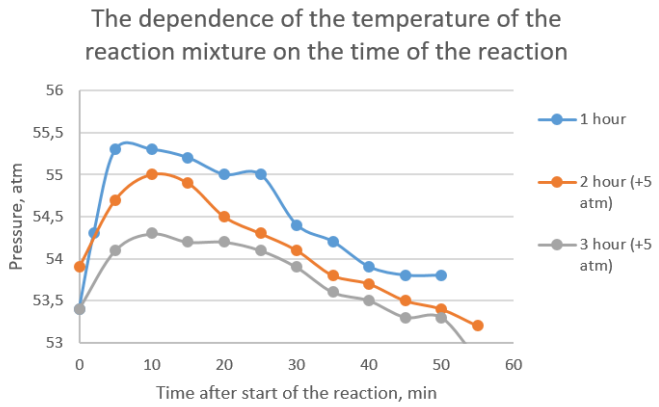
Conclusions

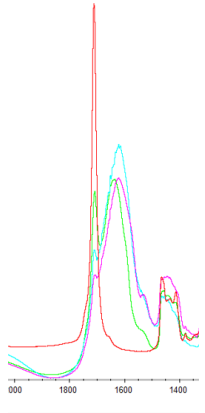
- Concentration of the oxygen does not influence on the rapid of the reaction

Kinetics and analysis









Fragment of the IR spectrum

Red line - raw material
Other lines – product of synthesis in a pressure reactor

Carbonyl number

Description

50 ml of 0.5 M hydroxylamine hydrochloride solution is placed in two glasses. Add 0.3-0.5 g of the test substance to one of them. Leave to stir for 30 minutes. The liberated hydrochloric acid is titrated with 0.2 alkali solution.

Formula for calculating mass% of carbonyl group

$$X = \frac{(a - b) * 0.0056 * 100}{g}$$

a - the volume of 0.2 M solution of alkali used for the titration of the sample, ml
b - the volume of 0.2 M solution of alkali used for a blank sample, ml
0.0056 - number of grams of carbonyl group corresponding to 1 ml of 0.2 M alkali solution, g
g - weight of the analyte, g

Results

Experiment	Carbonyl number	The theoretical maximum of the Carbonyl number	Yield %
Synthesis in a flask (air bubbling)	0	0	0
Synthesis batch reactor	3.2	9.9	33

Conclusions

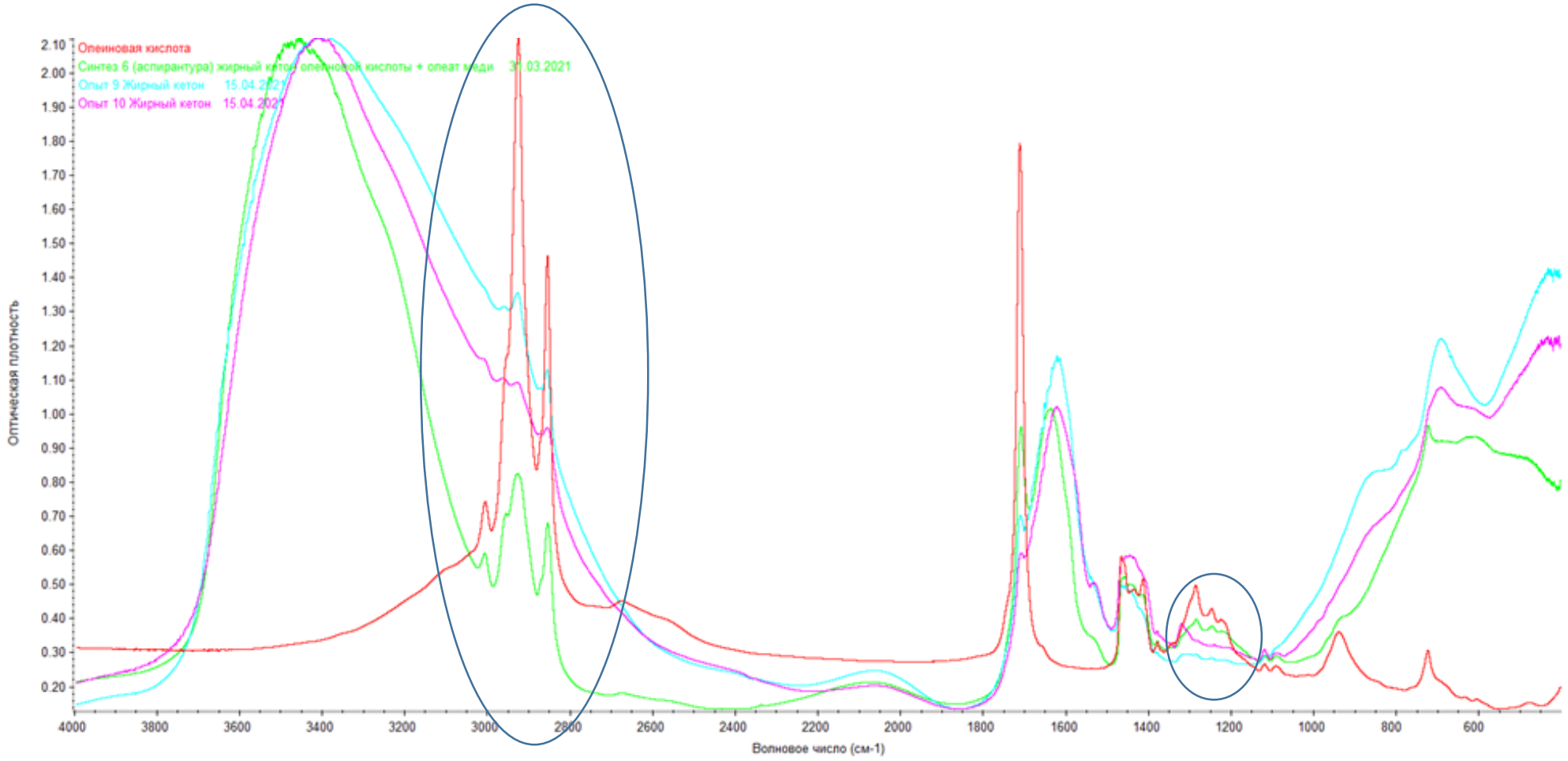
- The method for functionalizing double bonds of fatty acids and their derivatives into fatty ketones is proposed
- Industrial Waker-type process conditions are applicable for the opening of double bonds of fatty acids and their derivatives
- Zero order of reaction with respect to oxygen

Results

✓The method of synthesis is chosen

✓The course of the target reaction was confirmed by various physicochemical methods of analysis.

Thank you for your attention


Олеиновая кислота
Синтез 6 (аспирантура) жирный кетон олеиновой кислоты + олеат меди 31.03.2021
Опыт 9 Жирный кетон 15.04.2021
Опыт 10 Жирный кетон 15.04.2021
Оптическая плотность
Волновое число (см-1)