

# Synthesis of Glycerol Carbonate from Glycerol and Urea Using a Microwave Reactor

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Glycerol is a common byproduct of biodiesel industry and may be used as a starting material for the obtainment of different useful building blocks.

Among these, glycerol carbonate is one of the most valuable synthetic intermediates, due to its chemical features. A convenient, straightforward, and safe synthetic strategy for such a transformation involves the use of urea as carbonylation agent. The reaction is reported under Zn salts catalysis but, generally, long reaction times under heating are required.

As reported in literature, heating with microwaves can reduce reaction times and energy consumption. We thus studied the experimental conditions to obtain glycerol carbonate from glycerol under microwave heating, obtaining excellent yield and purity after screening process conditions and optimization of reactor's layout. The so-obtained glycerol carbonate is produced in multi-gram scale, with a purity grade that allows its use in further syntheses just after a simple solvent extraction as purification step. We also confirmed that the same results cannot be obtained with conventional heating.

## Introduction

The increasing attention to environmental sustainability of human activities led, in the last decades, to the fast growth of biodiesel industry [1]. The intrinsic advantage to obtain fuels from renewable resources comes from an improved neutrality on carbon cycle, as the CO<sub>2</sub> emitted during fuel combustion is reused during plants growth, the same being used for further biodiesel production [1].

Chemically, biodiesel is composed usually by methyl esters of fatty acids, obtained by methanolysis of triglycerides (**Figure 1**) [2]. As a result, glycerol is also formed as a byproduct. Thus, along with the relevant and fast growth of biodiesel

industry, equally relevant amounts of glycerol byproduct unavoidably begun to be formed. Its disposal as a waste is environmentally inconvenient, so its use as a starting material to give valuable building blocks was intensively studied in the last decades [3]. Many products can be obtained from glycerol, and among them one of the most valuable can be considered glycerol carbonate, due to its possible use as solvent, electrolyte, additive in many kinds of industrial formulations, or precursor for the synthesis of polymers, surfactants or chemical intermediates [4]. Three main methodologies are currently available to obtain glycerol carbonate from glycerol (**Figure 2**): (i) direct use of CO<sub>2</sub>, which could be ideally considered an optimal choice (atom economy), but suffers of poor yields and selectivity [5], (ii) transesterification with another carbonate, that suffers from low atom economy [6], and (iii) carbonylation with urea, a cheap and readily available reagent giving only ammonia as by product, that can be currently considered one of the most efficient and straightforward methods [7].

Anyway, the last option usually requires harsh conditions (high temperatures and long reaction times) [8], that hampers its attractiveness due to excessive energy requirements. New opportunities come from a recent report, describing the use of microwave heating to lower the reaction time and gain a better control over temperature, which renewed our interest in this synthetic option [9]. The reported procedure not only fits well our interests into the development of efficient and convenient methods for the synthesis of monomers, but is suitable to the multi-gram production of the same, a feature that let us to proceed with further investigations in polymer chemistry. In this paper we report our studies on the development of the method,

product purification, and possible further uses of glycerol carbonate from bio-based glycerol.

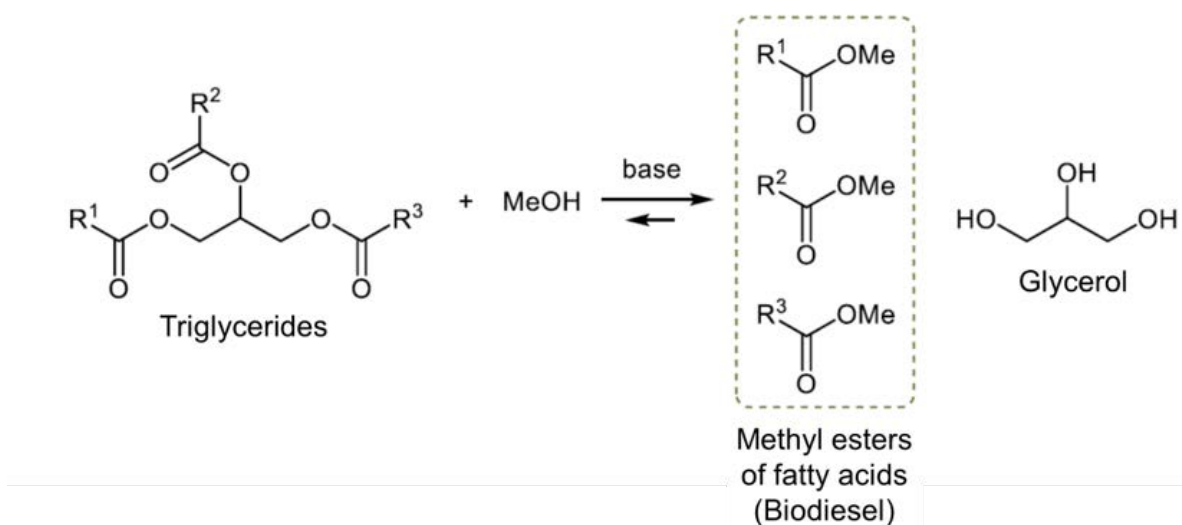


Figure 1. Methanolysis of triglycerides to give biodiesel and glycerol

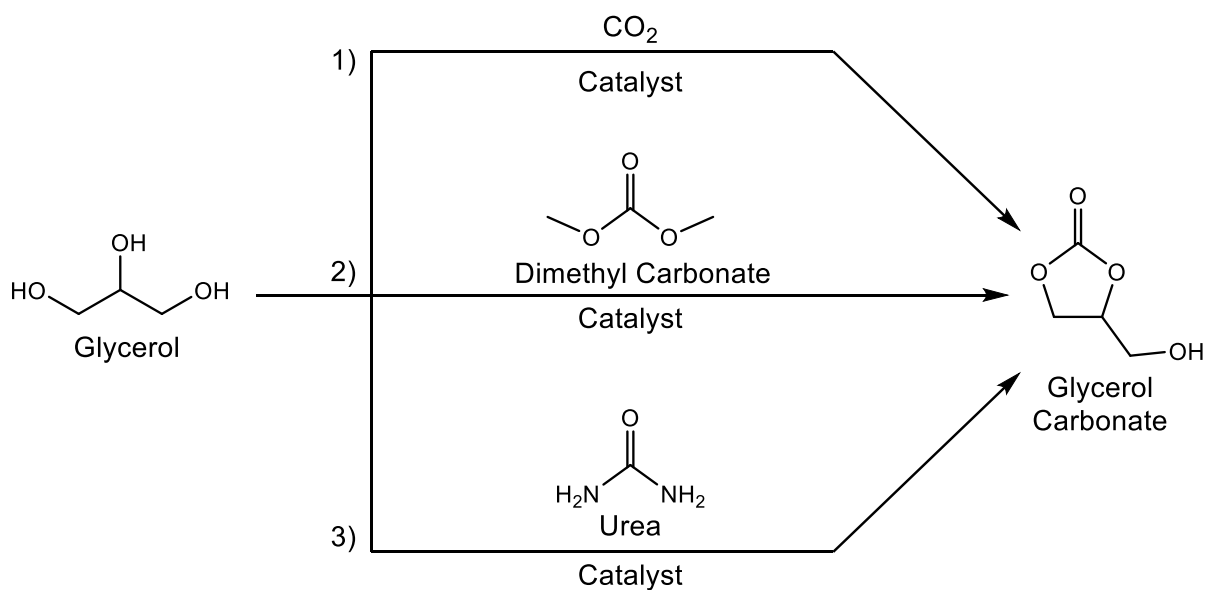


Figure 2. The three main synthetic pathways to glycerol carbonate using glycerol as starting material

## Results and Discussion

### Vessel setup

Based on the conditions reported in [9], we started an adaptation study to our microwave system (Milestone, mod. Ethos Touch) that, being different, required re-optimization.

Moreover, the cited paper did not give information about the reaction scale, which is very important in deciding which microwave power to use. By the way, we had already experience into working *in vacuo* with this system both in vessels and using a three necked flask [10-12]. On that occasion vacuum was used for solvent distillation, while here the need for vacuum is shifting the equilibrium towards products by removing ammonia, the reaction byproduct [9]. With a different aim, the optimal setup can be different from the previous cases and should be investigated.

It was decided to begin with a small amount of glycerol/urea mixture (8 g overall), using a glycerol:urea ratio of 1.25:1, and 3 mol% of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  as a catalyst, with the reaction carried

out in vessels (Table 1). It was soon realized that an excessive microwave power decompose the reaction mixture (Table 1, entry 1). Having gradually increased the amount of reaction mixture, a better temperature control was obtained. In the previous cases, temperature oscillations were very large which led to much higher than desired temperatures in the mixture experimented, promoting decomposition. In fact, just 3 minutes on 8 g at 150 °C (Table 1, entry 2) gave better results (yield and purity) with respect to longer times at lower temperatures using 10-12 g of mixture (Table 1, entries 3-4). Working with 15 g of mixture gave even better results, since it allows to work at 165 °C with moderate yield and purity (Table 1, entry 5), the latter increased by the use of  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  as catalyst (Table 1, entry 6). Apparently, the reason for these results is that working on a bigger scale allows a more accurate temperature control. Increasing vacuum grade, instead, led to urea sublimation and poorer yields (Table 1, entries 7-8).

Table 1. Screening of reaction conditions in vessel

Entry	Mixture amount	MW Power	Time (min.)	Temperature (°C)	Vacuum (mmHg)	Yield (%)	Appearance	Purity
1	8 g	600 W	20	150	-200	Decomp.	brown	-
2	8 g	175 W	3	150	-200	24	Yellow	Moderate
3	10 g	175 W	10	140	-180	18	Yellow	Low
4	12 g	175 W	10	145	-200	23	Yellow	Low
5	15 g	175 W	15	165	-200	33	Yellow	Moderate
<u>6*</u>	<u>15 g</u>	<u>175 W</u>	<u>15</u>	<u>165</u>	<u>-200</u>	<u>33</u>	<u>Yellow</u>	<u>High</u>
7	15 g	175 W	15	148	-350	18	Yellow	High
8	15 g	175 W	15	148	-500	27	Yellow	Low

Glycerol/urea = 1.25:1, catalyst:  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  3% mol. \*  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  3% mol was used as catalyst.

### Flask setup

Results reported in (Table 1, entry 6) were promising but still very far from the reported ones [9]. Therefore, it was decided to change the setup of microwave reactor and switched to a three-necked round-bottomed flask equipped with a mechanical stirrer, temperature probe and vacuum connection. This allowed us working in controlled conditions, especially regarding stirring, that

proved essential to improve homogeneity avoiding hot spots. This setup also let us to select the best temperature probe and to choose its most convenient position within the oven.

Firstly, it was decided to perform temperature control using a thermocouple placed above the mixture, in order to avoid its breakage eventually performed by the mechanical stirrer, as we did in our previous works [10-12]. Unfortunately, this

setup led to fast and extensive decomposition during our first test. We reasoned that in this case, the reaction environment was very different from what we had in our previous publications: in those cases we were working under vacuum to distill a solvent, so all the gas phase was full of the solvent vapors, also partially condensing on the thermocouple; moreover theory says that, during boiling, the solvent temperature in the liquid and in the gas phase is the same. In that case, therefore, measuring gas temperature above the liquid gave also a correct temperature for the liquid.

In the present case, there was no solvent, and gas phase is mainly air. Of course, air absorbs much less MW than glycerol, that has a very high  $\tan\delta$  [13], and so the reaction mixture was overheated with respect to air resulting in very high temperatures and mixture decomposition. Moreover, vacuum cools the air. To overcome this problem, it was realized that it was necessary to measure temperature directly inside the reaction mixture. In order to avoid accidental probe breakage, we chose for this operation a flexible optical fiber covered with Teflon. The use of this second probe allowed a proper reaction temperature control and gave much better results. In fact, if we compare the temperature/power profile of vessel

setup (**Figure 3a**) and of flask setup with this probe (**Figure 3b**) the stability of delivered power (black line) and of the temperature of the reaction mixture (green line) is much higher in the flask setup. Moreover, in **Figure 3b** the red line represents the temperature measured by the thermocouple probe, placed above the reaction mixture that confirms a much lower temperature of the air surrounding the liquid. Therefore, it is evident that controlling temperature in this position leads to a large overheating of the reaction mixture, clearly resulting in extensive decomposition of the same. This underlines the importance of directly measuring the temperature of the object one is heating, whenever possible, instead of its surroundings, when working with microwaves. The higher efficiency of the flask/optical fiber setup has been evident since the first test. A yield improvement was obtained by decreasing both the reaction temperature and the reaction time (**Table 2**) due to the better control of reaction conditions and less decomposition of the reaction mixture.



**Figure 3.** a) typical temperature (green line)/power (black line) profile when using vessel setup: intermittent power delivery leads to up to 10 °C temperature oscillation around the set value. b) typical temperature (green line)/power (black line) profile when using flask setup: a homogeneous power delivery leads to a stable temperature. Note the red line which is the temperature measured by the thermocouple.

**Table 2.** early conditions screening for the carbonylation of glycerol with urea using the three-necked flask setup.

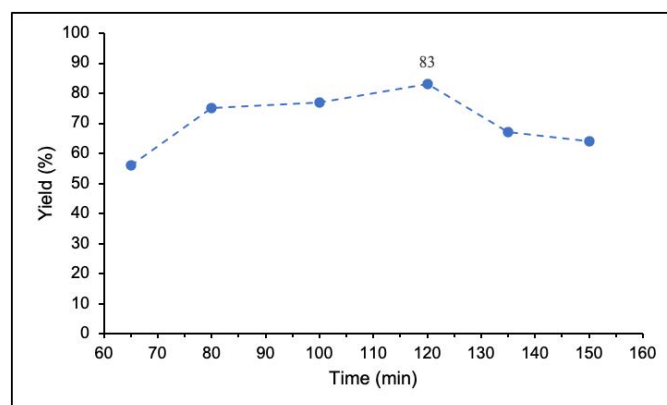
Entry	Temperature (°C)	Time (min)	Yield (%)
1	160	30	41
2	155	60	56
3	150	80	75

Urea/glycerol = 1.25:1; Mass of reaction mixture = 20.0 g; Catalyst:  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  3 mol %, Max Power: 175 W. Vacuum: -200 mmHg. Stirring speed: 450 rpm.

Therefore, it was decided to gradually increase the reaction time fixing all the other reaction conditions (please find them in **Figure 4** caption) to find finally an optimum reaction time of 120 min for this transformation to give an 83% yield of glycerol carbonate (**Figure 4**).

It is worth noting that, whereas in the reference paper a product purification procedure is not reported, all yields reported in this paper are isolated yields: the crude product was purified with a solvent extraction performed with a small amount of water and a 3:1 mixture of ethyl acetate/diethyl ether. The organic phase was then concentrated *in vacuo* to give the product with the purity given in **Table 1**, for the vessel setup. Anyway, when the flask setup was used, especially for the entries with the best yields seen in **Figure 4**, glycerol carbonate grade is higher, and can be considered acceptable for its use in further synthetic steps (see NMR spectrum in **Figure 5** for example). Other tedious and expensive purification steps can thus be avoided when this procedure is applied. The advantages gain with MW heating were revealed with a parallel experiment conducted with conventional heating. When a mixture of urea and glycerol (1.25:1 molar ratio), containing  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  (3 mol % with respect to glycerol) was stirred in a round bottomed flask at 150 °C (oil bath) for 120 min and -200 mm Hg, a yellow oil

was obtained. This, after solvent extraction, only gave a 15% yield in glycerol carbonate.



**Figure 4.** results of carbonylation of glycerol with urea using the three-necked flask setup at different reaction times. The other conditions were: Urea/glycerol = 1.25:1; Mass of reaction mixture = 20.0 g; Catalyst:  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  3 mol %, Temperature: 150 °C, Max Power: 175 W. Vacuum: -200 mmHg. Stirring speed: 450 rpm.

Glycerol carbonate obtained in multi-gram scale through MW heating could be used for further transformations, for example, in the synthesis of isocyanate-free polyurethanes (**Figure 6**) or others, currently under development in our laboratories. This approach is favored by the availability of large amounts of glycerol in the biodiesel industry.



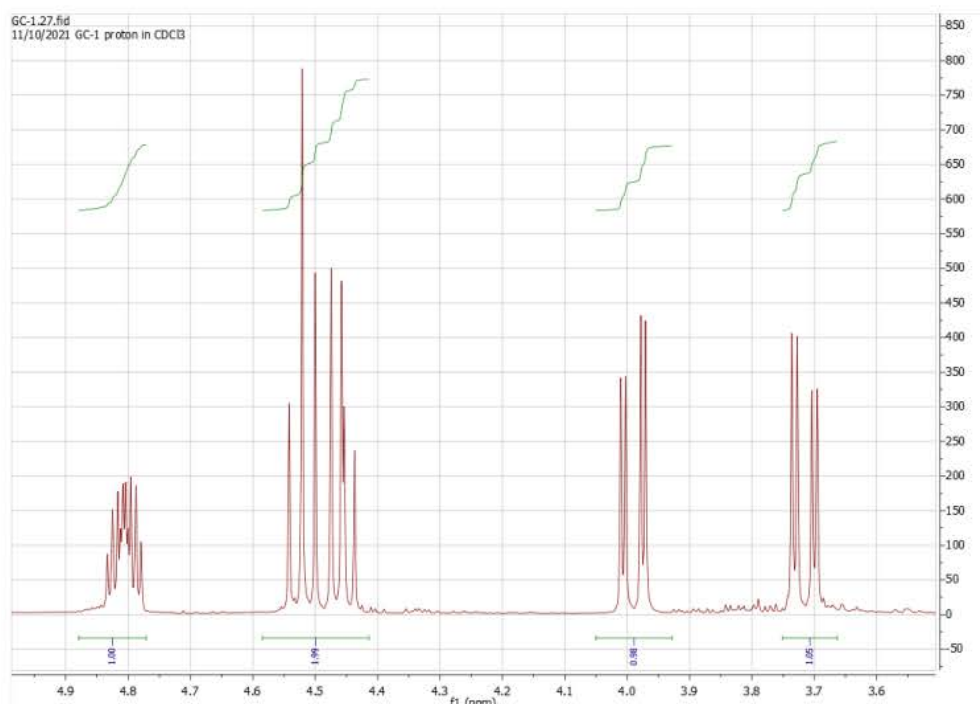


Figure 5. NMR spectrum of glycerol carbonate obtained in the 3<sup>rd</sup> test reported in Figure 4 (77% Yield) after solvent extraction.

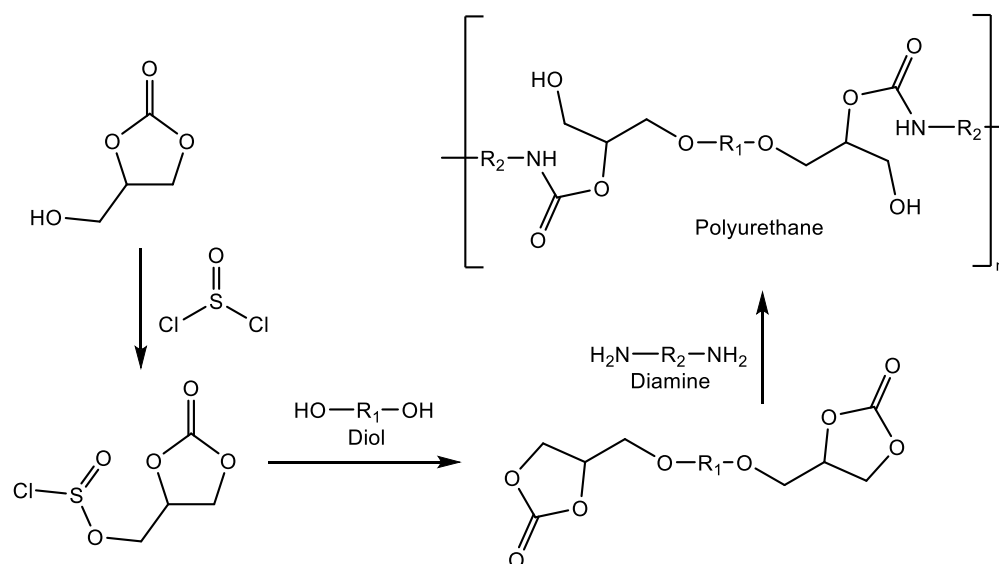


Figure 6. A possible isocyanate-free synthesis of polyurethanes using glycerol carbonate as starting material.

## Conclusions

In this paper, the carbonylation of glycerol with urea under microwave irradiation described in a previous report [9], was re-investigated, in order to evaluate the best reactor implementation as well as isolation and purification of the obtained glycerol carbonate.

It was found that the reaction carried out in vessels gave poor yields, while using a flask setup gave more satisfying results. The accurate

temperature control was essential: when the temperature was measured above the reaction mixture, a method very effective in other contexts, extensive decomposition of the reaction mixture occurred.

The employment of an optical fiber probe directly placed in contact with the mixture gave a substantial improvement. Mixture uniformity was very important too: flask setup equipped with magnetic stirring was superior to vessel setup. With

the optimal reactor, final screening of the conditions allowed to get 83% yield in glycerol carbonate.

Notably, this is an isolated yield after a simple water/organic solvent extraction giving a product featuring an acceptable purity grade for direct use in further organic transformations. The results reported in this paper reveal substantial improvement in terms of product yield and purity, when compared with a control experiment featuring conventional heating (same T and time).

### For further reading

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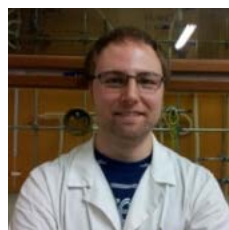
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### About the authors



**Gaia Romano** holds a Bachelor degree in Chemistry and is engaged in studies on sustainable chemistry. In continuing her academic career towards the master's degree she is interested in the development of innovative chemistry capable of giving added value to process wastes.



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**Roberto Rosa** is Associate Professor in Principles of Chemistry for Applied Technologies, at the Department of Sciences and Methods for Engineering of the University of Modena and Reggio Emilia. His research activity is focused on innovative and environmentally sustainable synthetic and processing strategies for advanced inorganic materials. His expertise also include the use and application of metrics, tools and methodologies for the quantitative environmental sustainability assessments of chemical products and processes.



**Cristina Leonelli** is Full Professor in Principles of Chemistry for Applied Technologies at the University of Modena and Reggio Emilia. Her field of interest is in solid state chemistry with particular interest in the reactivity of ceramic powders and transition from amorphous to crystalline state. She has a personal experience in designing new composition, preparation and characterization of different inorganic powders and bulk ceramic materials as well as application developments. She has also been active in the field of several innovative preparation techniques and

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## ***Microwave and Ultrasound Activity of CHEMSPEED Ltd. Romania – New Challenges and Opportunities***

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This year is representative for CHEMSPEED as we celebrate 15 years from the start of the activity in the field of microwave & ultrasound chemistry. All this period was exciting and fulfilled with new opportunities for the technological transfer for emergent technologies like microwave and ultrasound chemistry. Main domains of our activity are extraction of the active ingredients from vegetal biomass, microwave assisted pyrolysis of waste biomass, synergetic microwave & ultrasound synthesis of nanomaterials and several organic & inorganic compounds.

CHEMSPEED has developed multiple partnerships with national Universities and Research Institutions such as The Polytechnic University of Bucharest - Faculty of Chemical Engineering and Biotechnologies Department of Bioresources and Polymer Science and Faculty of Power Engineering; “Ilie Murgulescu” Institute of Physical Chemistry of the Romanian Academy; National Institute for Research & Development in Chemistry and Petrochemistry – ICECHIM; National Institute for Laser, Plasma and Radiation Physics – INFLPR; Banat University of

Agricultural Sciences and Veterinary Medicine of Timisoara – USAMVBT; National Research and Development Institute for Cryogenic and Isotopic Technologies – ICSI; international collaborations with: Microwave Technologies Consulting, Lyon, France; Department of Biological & Agricultural Engineering, Louisiana State University, USA; Sonochemistry Department of Coventry University, U.K.; SAIREM SAS, Lyon, France and much more.

CHEMSPEED’s main activity is based on technological transfer and industrial scale-up of the processes assisted by microwaves and ultrasounds. A few examples are: Sintchem Technologies Ltd. Romania – pilot plant for microwave-assisted extraction of rose essential oil from rose petals, Primosal Ltd., Romania – microwave-assisted synthesis of fire proofing products for wood and textile materials, Smartchem Solutions Ltd., Romania – microwave-assisted extraction of active ingredients from blackcurrant buds, walnut buds, rosehip buds, cedar branches for shampoo formulation with applications in the treatment of dry injuries from canine demodicosis, Activ Trade