

## THE ION-EXCHANGER UTILIZATION FOR SYNTHESIS OF MONOACYLGLYCEROLS

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### ABSTRACT

*Monoacylglycerols (MAGs) are being produced in considerable volumes (about 200 000 metric tons p.a.) at present. The reason for this is their extensive usage in the foodstuff industry in the first place. The employment of MAGs in pharmacy and humane medicine is even more important, particularly as components in gels enabling to deliver medicinal drugs to the organism(1).*

*This work is focused on the verification of the preparation possibility of lauric acid monoacylglycerol using the ion-exchanger resin Amberlite IRA-400(CI) (SIGMA-ALDRICH, Prague) as a catalyst. The chromium(III) acetate hydroxide (CAH) has been chosen as a co-catalyst because of its high catalytic efficiency and regioselectivity. The long-run goal is degreasing the content of residual chromium(III) ions in a final product. Due to the toxicity it was necessary to remove this catalyst from monoacylglycerols by the use of re-crystallization and former filtration of solid parts. It was found out that by combining the above mentioned catalysts it is possible to reach the high conversions (more than 95%) and significant selectivity of the reaction. This method can simultaneously several fold decrease the amount of chromium entering the reaction.*

**Key words:** Monoacylglycerols, ion-exchanger, chromium(III) ions

### 1. MATERIALS AND METHODS

MAGs of lauric acid were prepared in an open glass reactor provided with magnetic stirrer and temperature-stabilizing jacket enabling to maintain the temperature of mixture to an accuracy of 0.5°C. The preparation of MAGs consisted in melting a known quantity of acid (approx. 5g of lauric acid) in an already heated reactor (mostly 90°C) and subsequent adding a known quantity of a catalyst and glycidol. At selected time intervals a sample of the molten reaction mixture was withdrawn and analyzed for the content of unreacted acid by titration with 0.1M ethanolic KOH solution to phenolphthalein. The conversion (X %) of fatty acid was calculated from the arithmetic mean of four acid-base titrations and expressed as %X = 100 - %C where %C is given by the equation (1).

$$\%C = \frac{a \cdot c_{\text{KOH}} \cdot M_k}{1000 \cdot m \cdot p} \cdot 100 \quad (1)$$

where  $a$  is the consumption of 0,1M ethanolic KOH solution (ml),  $c_{\text{KOH}}$  is concentration of KOH solution (mol.l-1),  $M_k$  is the molecular weight of lauric acid (g.mol-1),  $m$  is weight of the sampled MAG (g),  $p$  is the ratio of real fatty acid charge put into the reaction and total weight of all reactants.

The chromium content in monoacylglycerols was monitored after the previous mineralization of samples ( $\text{HNO}_3 + \text{H}_2\text{O}_2$ ) by atomic absorption spectroscopy (AAS). Selectivity of reaction was detected by thin-layer chromatography and gas chromatography with mass detection. Densitometry was used for semi-quantitative evaluation.

## 2. RESULTS

Reaction parameters optimization (see Figures 1 - 3) and an example of densitometric analysis of sample MAG (Figure 4).

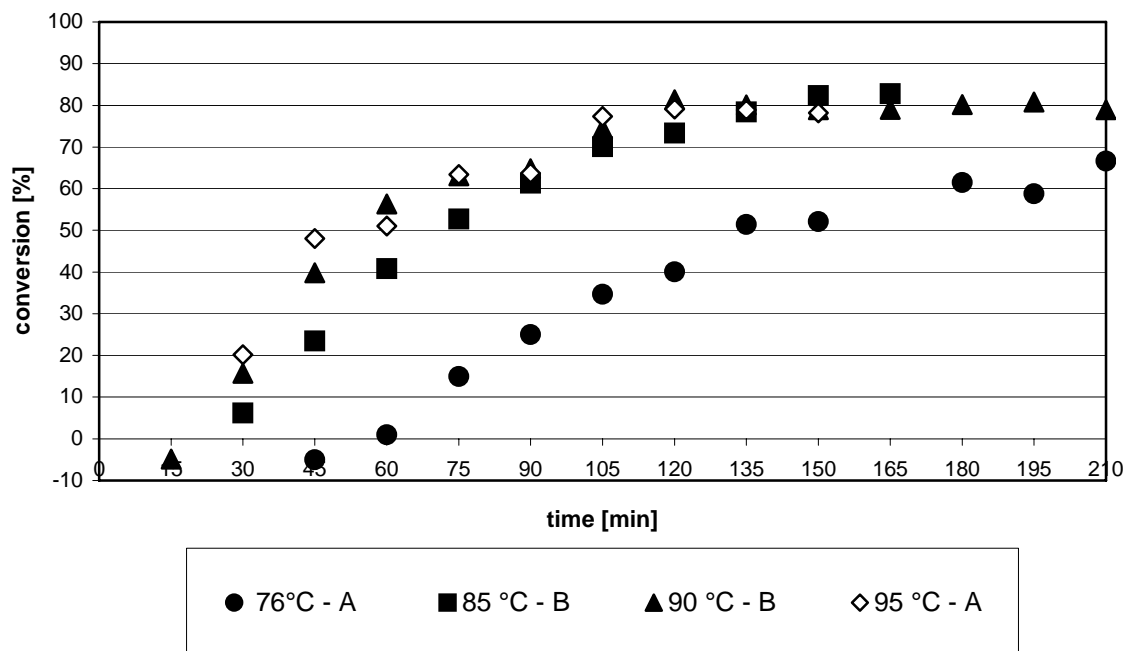


Figure 1. Graph of the reaction conversion dependence on time at various temperatures ( $p = 0,69$ ,  $m_{\text{Amberlite}} = 2 \text{ g}$ , molar ratio of acid : glycidol 1 : 1,2).

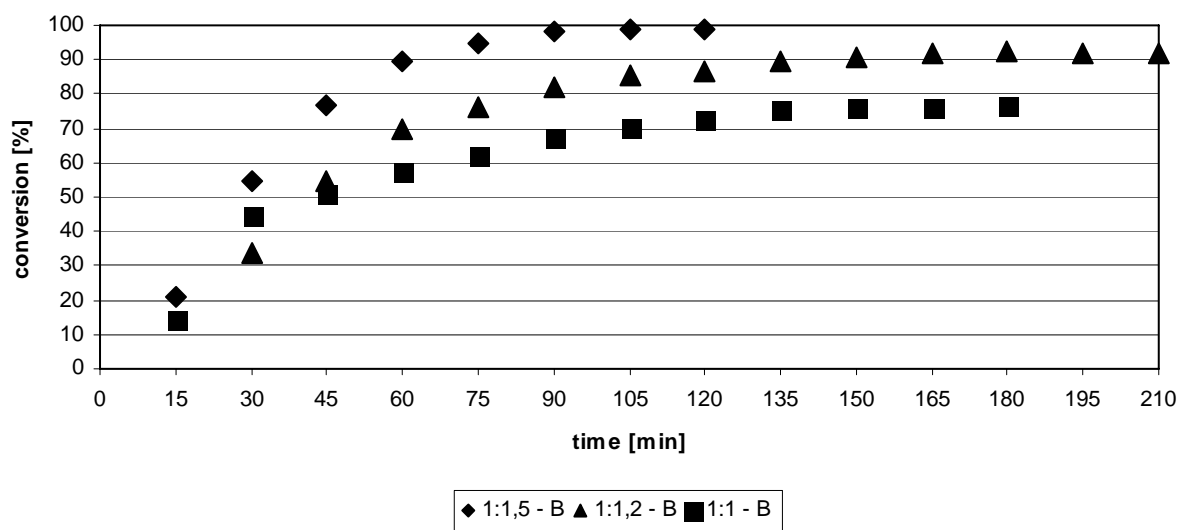


Figure 2. Dependence of reaction conversion on time at different molar ratio of reactants ( $t = 90 \text{ }^\circ\text{C}$ ,  $m_{\text{Amberlite}} = 2 \text{ g}$ , 0,1 % CAH).

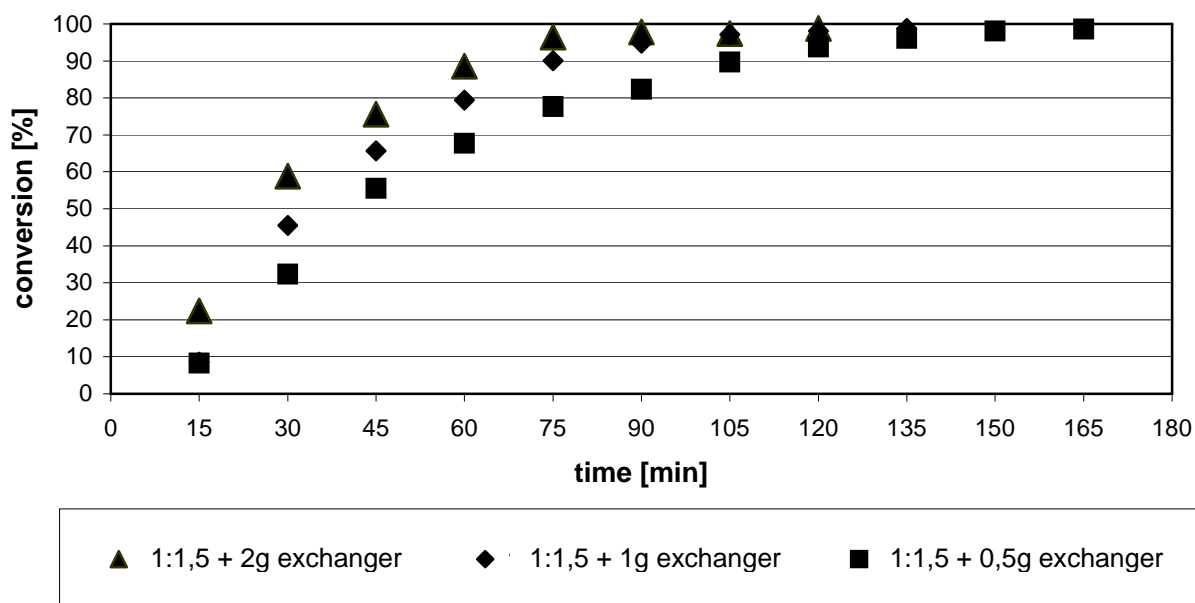


Figure 3. Graph of the reaction conversion dependence on time at the ratio of 1 : 1,5 (acid : glycidol) and various ion exchanger amounts ( $p = 0,64$ ,  $t = 90$  °C, 0,1 % CAH ).

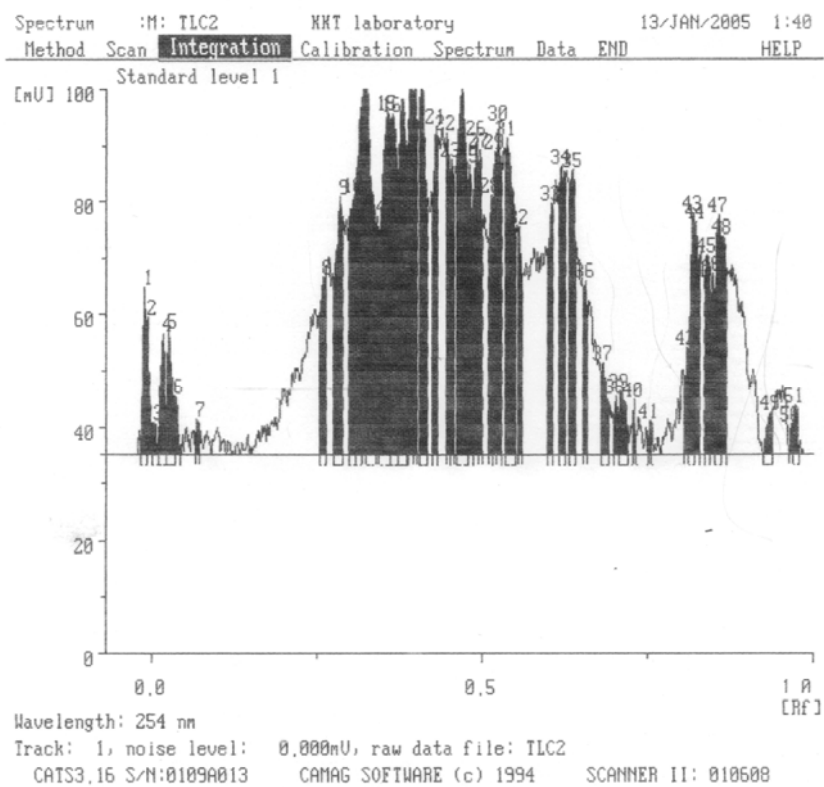


Figure 4. Densitometric analysis of lauroylglycerol sample of 95% conversion.

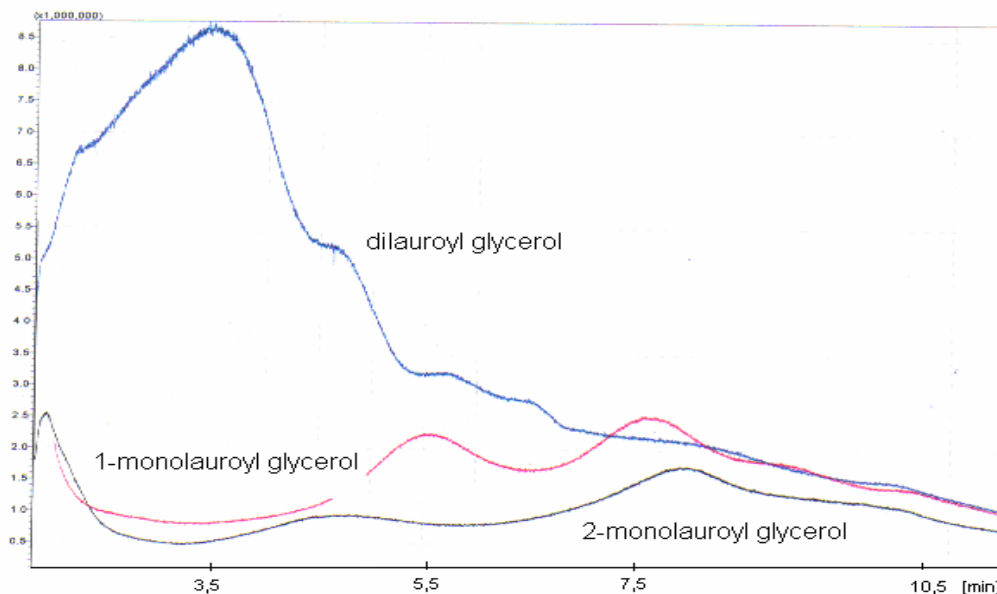


Figure 5. GC chromatogram of acylglycerols

### 3. CONCLUSIONS

- It was verified that it is possible to use Amberlite-IRA 400 (Cl) as an effective heterogeneous catalyst for the addition reaction of glycidol and lauric acid. Using the ion exchanger in the amount of 40 % (related to lauric acid amount) the conversion up to 80,81 % can be obtained in 3 hours.
- TLC analysis proved that 2-monolauroylglycerol and 1,2(1,3) dilauroylglycerol are also produced beside 1-monolauroylglycerol.
- The reaction selectivity and maximum conversion can be improved by the CAH addition used in the combination with the ion exchanger. Due to the combination of these catalysts it is possible to reduce the CAH amount even 50-times compared to the experiments when CAH was used as the only catalyst and to reach the conversions approaching up to 100 %.  $\text{Cr}^{3+}$  (AAS) content is lower than 80 mg/kg of a product.
- Densitometric semi quantitative analysis revealed that the ratio of 1-monolauroylglycerol and 2-monolauroylglycerol is 8,74 : 1,26 in the sample with the conversion of 95,3 % (see Figure 4).
- Using the mass spectrometry the prevailing substance in the product like 1-monolauroylglycerol was successfully identified (see Figure 5).
- Optimization experiments revealed that the maximum conversion of 99 % can be obtained in 180 min at the temperature of 90 °C, 50 % molar excess of glycidol toward acid, 10 % ion exchanger charge and 0,05 % CAH related to the acid amount.

### 4. ACKNOWLEDGMENT

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### 5. REFERENCE

- [1] JANIŠ, R., KLÁSEK, A., BOBÁLOVÁ, J.: Chromium(III) acetate hydroxide – an Efficient Catalyst of the Glycidol - Fatty Acids Reaction. *J. of Food Lip.*, 2006, Vol 13, No 2, 199-209, ISSN 1065-7258