

Alkoxylation for surfactant productions: towards the continuous reactors

NIGL NICL- Naples Industrial Chemistry Laborato



NICL- Naples Industrial Chemistry L

Introduction

The alkoxylation reactions are generally performed in semibatch reactors [1] in which the catalyst and the substrate (alkyl phenols, fatty alcohols or acids) are initially charged while epoxide (ethylene or propylene oxide) is added during the reaction course. This particular synthesis strategy is due to the high reactivity of alkoxides and also to the high heat involved in alkoxylation reaction. The use of semibatch reactors, however, have some drawbacks that can be summarized in the following points: (i) the reactor volume is relatively high;

(ii) the productivity of the system is quite low for the various steps involved in a semibatch process

A possible solution that could allow to overcome the mentioned drawbacks is the adoption of a continuous reactor

Continuous reactors

Coiled, microreactors and falling film multiple pipes

The first results have been obtained by using tubular reactors, working under optimized process conditions of pressure and temperature.

Even achieving high space-time yields, there are problems in the thermal control of the system. This fact has been solved by diluting the ethylene oxide concentration by splitting the feed at different points along the tubular reactor. This solution lead to drawbacks and difficulties due to the necessity of a very complex process control system, particularly in the case of high numbering-up (replication of multiple modules). *mol%

Reactor	Alcohol	С _{сат} , %	Alcohol/ Alkoxyde	<i>Т_{мах},</i> °С	τ, s	P, kg/(hm³)	Ref.
Coiled tubes	C ₁₂₋₁₄	0.10	1:1-1:6 mol/mol	287	25	120000	2
Coiled tubes	Sucrose	0.40	11.4:5.8 w/w	180	600	-	4
Micro- channels	Octanol	0.66*	1:3-1:6-1:9 mol/mol	240	50	12600	3
Falling film multipipe	n-nonyl phenol	0.60	1:7 mol/mol	220		22000	5
Micro- reactor	Butanol	5.00	1:9 mol/mol	150	300	-	6

Microinnova alkoxylation plant



Microinnova Engineering GmbH solved the problem of the low productivity of micrometers using a microstructured chemical reactor developed by the Institut für Mikrotechnik Mainz (IMM) GmbH with innovative fabrication techniques [7]. The reactor is built with the concept of modularity which allows the manufacture of different reactors according to the requirements of the process

<u>Coiled reactors</u>: suggested in the pioneering work of Umbach and Stein [2]. The authors were able to obtain a complete conversion of alkoxydes in very short residence times, in the range 15-150 s, much lower than discontinuous processes. Even if only reactions with low alkoxylation degrees were tested in this investigation (2-4 moles of alkoxyde per mole of substrate), the productivities obtained resulted very interesting, giving place to a product throughput up to 100-120 kg/h that corresponds to a monthly production of 60-70 ton and with a specific productivity of 120000 kg/(h m³). The same concept has been developed, for sucrose based polyethers production, in the patent by Hinz et al. [4] Experimental conditions: P=60-100 bar, T=60-70 °C, L/D=1400-2500, T_{MAX}=240-300°C (Fig. 1).



Microreactors: Rupp et al. [3] studied octanol ethoxylation by using a single microchannel reactor immersed in a thermostatic bath. These authors performed an extensive experimental and modeling investigation on the possibility to continuously produce ethoxylated octanol, to a various degree, in a short residence time (50 s) with an ethoxylation degree on octanol in the range 3-9 and a productivity of 12600 kg/(h m³). Thermal profiles were under control (Fig. 3). Experimental conditions: P=90-100 bar, T=130-240 °C, L/D=2000-4600.

Falling film multipipe: the reactor is designed as a concentric tubular reactor in which an annular space is obtained for performing the reaction continuously [5] (Fig. 3). In this way the annular gap reaction volume is very similar to a thin film with enhanced properties of thermal exchange and able to achieve safe operation. Such a reactor system is characterized by a L/D ratio of about 770 and is able to achieve a product throughput of 250 kg/h (7 moles of EO per mole of n-nonyl phenol) in correspondence to a residence time of roughly 160 s and with a productivity of 22000 Kg/(h m³).Despite this reactor was built in a quite complex way, it open the perspective of a real industrial utilization in the field of alkoxylation technology.

Conclusions

A promising perspective is nowadays available for performing alkoxylation reactions in continuous modality. It has been demonstrated that specifically designed continuous reactors can furnish very good performances in terms of productivity and for ensuring safe operation in the adopted conditions. The reactors are characterized by sufficient flexibility to achieve different alkoxylation degree being, in this way, suitable for different productions. The obtained productivity are sufficiently high to guarantee, also considering reactor modularity, the possibility of useful industrial applications. Employing these emerging technology, a new era in alkoxylation technology could start in a near future.

Cited Literature

- mical substances with active hydrogen atoms, US0289315A1 (2013)
- M. Di Serio, R. Tesser, E. Santacesaria, Comparison of Different Reactor Types Used in the Manufacture of Ethoxylated, Propoxylated Products, I&ECR 44 (2005) 9482-9489.
 W. Umbach, W. Stein, Continuous Alkoxylation Process, JAOCS 48 (1971) 394-397
 M. Rupp, W. Ruback, E. Klemm, Octanolethoxylation in microchannels, Chem. Eng. And Proc. 74 (2013) 19- 26
 W. Hinz, E. M. Dexheimer, Continuous process for the production of sucrose based polyether polyols, US6380367B1 (2002)
 R. Algner, D. Hirsch, A. Lagnaz, Process and apparatus for continuous high temperature short-time alkoxylation (ethoxylation, propoxylation) of chemical substances with active F
 R. Hubel, G. Markowz, M. Recksik, M. Rudek, D. Wewers, F. Zeller-Schuldes, Alkoxylation in microstructured capillary reactors, US785882982 (2010)
 H. J. K. K. B. K. Decknik, M. Schwar, M. Schwark, M. Stehen, M. Stehen, M. Stehen, D. Huber, M. Schwark, M. Schwark [7] U. Krtschil, C. Hofmann, P. Lob, C. Schutt, P. Schorcht, M. Streuber, Novel Manufacturing Techniques for Microstructured Reactors in Industrial Dimensions, Green Process Synth (2013) 451-463