**Overall Reaction Rate of Oximation of Impurities in the Production Process of Caprolactam.**

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**Highlights**

* Impurities oximation using hydroxylamine sulfate as reagents.
* Reaction routes the main impurities formed in the caprolactam production process.
* Kinetic models of oximation reaction the main impurities in cyclohexanone.

**1. Introduction**

Caprolactam is used as a monomer in the nylon 6 production process. The most common caprolactam production process is promoted by oxidation of cyclohexane to obtain a reaction mixture known as KA-oil, which contains cyclohexanone, cyclohexanol and other impurities [1-3]. Cyclohexanone, after being purified, reacts with hydroxylamine, and subsequently epsilon-caprolactam is [obtained by Beckmann rearrangement of cyclohexanone oxime](http://www.google.es/patents?hl=es&lr=&vid=USPAT4806638&id=f3JMAAAAEBAJ&oi=fnd&dq=Beckman+oxime&printsec=abstract) [4]. The quality of the nylon 6 fibers is closed affected by type and amount of the impurities presented in ɛ-caprolactam. Leading companies in the production sector are currently examining the origin and the development of those impurities, to reduce their formation or to promote their elimination. The characterization of the quality of the ɛ-caprolactam, by means of the quantification and identification of its impurities is a complex task. Main difficulties in the determination of the impurities are their variety, low concentration and lack of information due to the confidenciality of the processes. Based on available information in literature the main impurities in cyclohexanone that could be transformed in the oximation step affecting the quality of ε-caprolactam have been selected. The scope of this work is the study of the transformation of these impurities found in the pure cyclohexanone in the oximation reaction step.

**2. Methods**

The impurities selected were n-heptanones (n=2,3), hexanal, n-methylcyclohexanones (n=2,3,4), 2-methylcyclopentanone, 2-cyclohexen-1-one. These ketones are in appreciable amounts in the purified cyclohexanone and have significant negative effects on the final nylon 6.

The oximes of these impurities were synthesized from their commercial ketone. They were identified by NMR and gas chromatography using a mass detector (GC/MSD) to obtain the stereoisomeric proportions that is produced in the oximation reaction. Oximation runs were carried out in an isothermal semicontinuous stirred reactor where NH3 solution was continuously fed to neutralize the acid promoted to keep a constant pH. The reactions were carried out using hydroxyl ammonium sulfate as reactant (82$ ℃$, atmospheric pressure and pH 5,5). In addition, it was studied the oximation reaction kinetics of those impurities that are in higher concentration in pure cyclohexanone or have greater effect on the quality of ɛ-caprolactam. The experimental conditions used were closed to the industrial. The kinetic study of 2-heptanone, 2-cyclohexen-1-one and 2-methylcyclohexanone was carried out. Samples were taken at different reaction times to quantify the amount of reacted ketone.

**3. Results and discussion.**

A kinetic model was proposed to obtain an overall oximation rate, under the industrial operation conditions. The model was developed assuming the reaction takes place in the interphase of the organic and aqueous phases and it does not exist mass transfer limitations at each phase, because of the high agitation used. Good agreement between experimental and predicted values was found, which means to validate the model proposed and the model assumptions. The model proposed can be summarized as follows:

$\frac{dX\_{ONA}}{dt}$ = $ S·k\_{ap} \frac{(1-X\_{ONA})}{V\_{org}}\left(\frac{N\_{SHA\_{0}}-1/2 (N\_{ONA\_{0}}(1-X\_{ONA}))}{V\_{aq}}\right)^{1/2} ∴ k\_{ap}^{'}$ = $\frac{ S·k\_{ap}}{V\_{org}}$ Eq.(1)

An apparent kinetic constant was proposed including the kinetic constant of the oximation rate of each respective impurity and the pH influence. In Table 1 the values of the apparent kinetic constant at 82 ºC and pH=5.5 are listed. It was found up that the oximation rate of 2-cyclohexen-1-one is the lowest one, followed by 2-heptanone, and finally, 2-methylcyclohexanone, whose apparent constant doubles the value of the 2-heptanone constant.

Table 1. Apparent constant values for the model proposed in Eq.1

|  |  |  |  |
| --- | --- | --- | --- |
| Compund | $$ k\_{ap}^{'}$$(kgaq0,5·mmol-1,5·min-1) | SQR | % VE |
| 2-heptanone | 0.033$\pm $0.002 | 0.098 | 96 |
| 2- methylcyclohexanone  | 0.066$\pm $0.006 | 0.078 | 97 |
| 2-cyclohexen-1-one | 0.0057$\pm $0.0003 | 0.120 | 97 |

**4. Conclusions**

The importance the quality of caprolactam has been increased last few years due to development of new technologies. However, the information about the impurities which can affect the quality of the final product is limited. In this work, the main impurities present in the cyclohexanone used as intermedia in the caprolactam process were synthesized and identified by GC/MS and NMR. Besides a kinetic model of the most important impurities was proposed. Kinetics constants obtained provide helpful information useful for the analysis of the purification steps.

**References**

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