Original Research Article

Synthesis and Characterization of Oleamide Slip Agent

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ABSTRACT

The present paper explores a new economical method for the synthesis of oleamide form the oleic acid and urea in the presence of catalyst at atmospheric pressure. Oleamide is mainly synthesized by ammonolysis of fatty acid or esters with ammonia gas at high pressure. Yet, using the urea instead of ammonia gas provides an economical reaction at atmospheric pressure. The structure of synthesized oleamide was characterized by FTIR analysis. The effect of oleic acid / urea molar ratio, time and temperature of reaction as well as amount of catalyst on the acid values or conversion of reaction was studied. The optimum condition for the synthesis of oleamide from oleic acid and urea was obtained to be oleic acid / urea molar ratio of 1:4, temperature of 200 °C and time reaction of 180 min with 1 wt% catalyst concentration. At this condition the acid value of 56 was achieved. Also, the reaction mechanism and kinetic were investigated in which ammonolysis followed pseudo-first order kinetics.

Keywords: Oleamide, Slip Agent, Oleic Acid, Urea, Kinetic.

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Introduction

Fatty acid amides are a main group of surfactants that have find different applications based on their physical properties. They are generally used as slip agent, lubricants, anti-block agent and detergents [1–3]. Fatty acid amides antiblock and anti-slip agents are used in polyolefins film during processing to reduce coefficient of friction (COF) [4]. Oleamide (*cis*-9-octadecenamide) is one of the popular unsaturated fatty acid amides, which is widely used as an industrial slip agent in the polymer manufacturing [5-6].

Since then, there has been a growing interest for developing new method for its synthesis. Typically, oleamide is obtained from animal sources [7]. However, fatty acid amides and especially oleamide have been produced by various methods through the reaction between ammonia and corresponding fatty acid, anhydride or lower alkyl esters at high pressure and temperature. The most common method for chemical synthesis of fatty acid amides is the reaction between ammonia and acids at 180-220 °C and 345–690 kPa as follow [8]:

$$RCOOH + NH_3 \rightarrow RCONH_2 + H_2O \tag{1}$$

$$RCOOH + RNH_2 \rightarrow RCONHR + H_2O \tag{2}$$

This method is expensive due to the high cost of raw materials. Also, the yield of the reaction between acid or anhydrides and ammonia gas is low, especially in the presence of fatty acid with higher carbon atoms. In addition, the operation condition of reaction is harsh, such as long reaction times and high pressure and temperature. At long reaction time, the dehydration of fatty acid amides to nitriles as a competing reaction is occurred [9-10].

Short reaction time is necessary to avoid the undesirable side reaction and by-product. Consequently, achieving to a desirable method with low cost, high yield and mild operation condition is inevitable.

Accordingly, the presence of catalyst in the reaction of fatty acids with ammonia gas leads to improved operational condition such as short reaction time and reduced pressures. Various researchers have been used alkyltin, hydrated titanium, zirconium and tin oxide [11-12] catalyst in amidation reaction of fatty acid amides with ammonia and studied the effect of catalyst and operational condition on the reaction conversion especially for erucamide synthesis. Some of

these processes still require high pressure (100 kPa to 1000 kPa) and high temperature (120°C-240°C) to achieve a desirable yield.

In view of raw materials, fatty acid and ammonia are the most commonly used material. However, replacement of ammonia gas with urea allows the amide synthesis at atmospheric pressure and it is more economical.

Hence, the aim of this work is to provide new method for the synthesis of oleamide by using the urea instead of ammonia gas in the presence of catalyst under mild condition and short reaction time. For this purpose, the effect of various parameter such as oleic acid / urea molar ratio, time and temperature of reaction as well as the catalyst concentration on the acid values of final reaction mixture are studied for the first time and optimum condition is explored. Also, the kinetic and mechanism of amidation reaction are evaluated. To the best of our knowledge, there is no comprehensive report on the synthesis of oleamide with urea and investigating the effect of operational condition on its conversion.

Experimental

Material

Oleic acid (Ali shimi, Iran) (Table 1) and urea (Shiraz Petrochemical Co., Iran) were used as the main raw materials. Aluminium chloride ($AlCl_3$) was purchased from Merck Co. as catalyst without further purification. Chloroform, n-hexane and acetonitrile from Merck Co. and ethanol from Harmun teb were used in purification process.

Table 1. property of oleic acid

Material	Property	Value
Oleic acid	Acid value	198.6
	Saponification value	196
	Iodin number	85.6

Synthesis of oleamide

synthesis of oleamide was carried out in a round bottom flask under reflux condition. Oleic acid, urea and desired amount of $AlCl_3$ catalyst were charged into the reactor. The reactor was heated and reaction was proceeded in controlled temperature and time. By heating the material, the urea was melted at 140℃ and will be decomposed to CO_2 and NH_3 at higher temperatures. During the

reaction and at the end of reaction, several samples were withdrawn at specified time and their acid values (AV) were measured. The reaction progress was defined by the final reaction mixture acid value in which, a decrease in the acid value confirmed the synthesize of fatty acid amide. To investigate, the effect of oleic acid / urea molar ratio, time and temperature of reaction as well as catalyst concentration on the reaction mixture acid value, the reaction was carried out with different molar ratio of component and operational condition according to the Table 2.

Table 2: Recipes for the synthesis of oleamide under different conditions

Experiment number	Oleic acid / urea molar ratio	Temperature (°C)	Reaction time (min)	Catalyst concentration (wt%)
1	1:1	200	180	1
2	1:2	200	180	1
3	1:4	200	180	1
4	1:5	200	180	1
5	1:4	160	180	1
6	1:4	180	180	1
7	1:4	200	60	1
8	1:4	200	120	1
9	1:4	200	240	1
10	1:4	200	180	0.4
11	1:4	200	180	0.8
12	1:4	200	180	1.2

Purification of oleamide

To purify the product, chloroform was added to the sample of previous step for solvent extraction and any excess urea was filtered. After that, the solvent was evaporated in oven at 70 °C. Then, the prepared crude oleamide was purified by a following sequence series of recrystallization with n-hexane, ethanol and acetonitrile solvents. For this purpose, Firstly, solvents were added to the sample of previous step and then pure oleamide was obtained from the solution.

Characterization

Chemical structure of the synthesized oleamide was investigated by FTIR analysis by using the KBr pellets (Bruker, USA).

The acid values (AV) of the reaction mixtures were calculated by a simple titration method as the amount of KOH (mg) required for neutralization of free acid in 1 g of sample.

$$AV = \frac{V_{eq} \times N \times 56.1}{W}$$
(3)

where, V_{eq}, N, 56.1 and W are titrant value, normality of KOH, molecular weight of KOH and mass of the sample, respectively.

Results and Discussion

FTIR spectra of oleamide

The FTIR spectrum of synthesized oleamide is shown in figure 1. The absorption peak of C=C groups is appeared at 1658 cm^{-1}. The broad peak at 3163 cm^{-1} is assigned to –NH$_2$ groups. The peaks at 2825 cm^{-1} is associated to methyl and C=O groups. Also, the peaks at 1454, 1358 and 1055 cm^{-1} are corresponded to C-H groups of alkene [12]. These characteristic peaks confirm the chemical structure of synthesized sample and match with the standard spectra of oleamide [13].
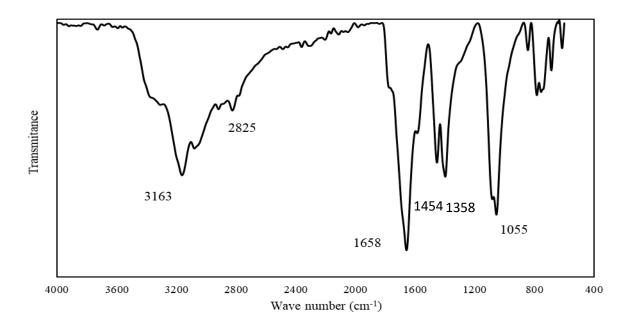

Figure 1. FTIR spectrum of synthesized oleamide

Effect of molar ratio of oleic acid / urea on the acid value

The effect of molar ratio of oleic acid / urea on the acid value of the reaction mixture was studied at various molar ratios of 1:1, 1:2, 1:4 and 1:5 by using 1 wt% of AlCl$_3$ catalyst at a reaction time of 3 h. (figure 2).

As seen, the AV values of reaction mixture were decreased from 73 to 55 by increasing the molar ratio of oleic acid / urea from 1:1 to 1:5. Nevertheless, the AV value of reaction mixture with oleic acid / urea molar ratio of 1:5 (i.e. AV:56) is close to that of with 1:4 molar ratio (i.e. AV:55). Therefore, further increase in oleic acid / urea molar ratio dose note have significant effect on the AV value and yield of reaction and the oleic acid / urea molar ratio of 1:4 is considered as optimum values for synthesis of oleamide. At this condition the conversion of oleic acid to reaction product is about 72% based on acid value.
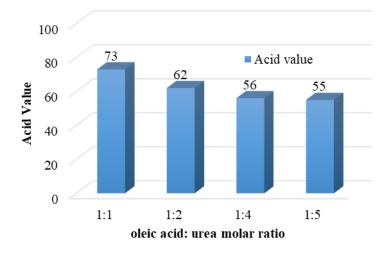

Figure 2. The effect of oleic acid: urea molar ratio on acid value at 200 °C and 180 min reaction time in the presence of 1 wt% $AlCl_3$

Effect of temperature on the acid value

The effect of temperature on the AV values of final reaction mixture was evaluated at three different temperatures (i.e. 160, 180 and 200 °C) for reactions with oleic acid / urea molar ratio of 1:4 by using 1 wt% of catalyst and a reaction time of 3 h (figure 3). As seen, temperature has a positive effect on the reaction progress and conversion of oleic acid to oleamide.

An increase in the reaction temperature from 160 °C to 200 °C led to a decrease in AV value from 66 to 56. The AV value is minimum at temperature of 200 °C and is considered to be the optimum temperature for the reaction.
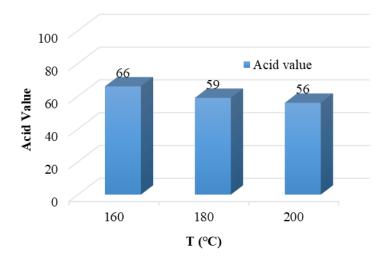
Figure 3. The effect of temperature on acid value at oleic acid: urea molar ratio of 1:4 and 180 min reaction time in the presence of 1 wt% $AlCl_3$

Effect of reaction time on the acid value

The influence of time on the acid values of reaction mixture at oleic acid / urea molar ratio of 1:4 and temperature of 200 °C is shown in figure 4. As seen, by increasing the time from 60 min to 240 min, the AV values of reaction mixture is declined from 107 to 53 and reached to a constant value. Comparison the AV values at reaction time of 180 and 240 min indicates that further increase in time does not give an appreciable effect on the AV values and ammonolysis reaction is completed within 3 h.
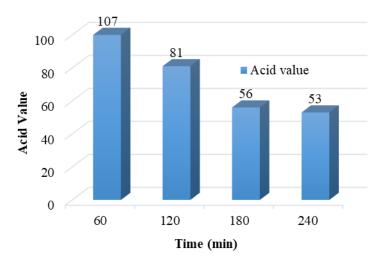

Figure 4. The effect of reaction time on acid value at 200 °C and oleic acid: urea molar ratio of 1:4 in the presence of 1 wt% $AlCl_3$

Effect of catalyst concentration on the acid value

To investigate the effect of catalyst, different concentrations of $AlCl_3$ catalyst, *i.e.* 0.4, 0.8, 1 and 1.2% were used in reaction with oleic acid / urea molar ratio of 1:4, temperature of 200 °C and reaction time of 180 min (figure 5). The results show that AV values and reaction conversion enhance with increasing the catalyst concentration. However further increase in catalyst concentration doesn't have any significant effect on the reaction yield. Therefore, the catalyst concentration of 1 wt% is selected as optimum concentration. As mentioned in before section, at this condition, conversion of reaction is 72% based on the acid value.
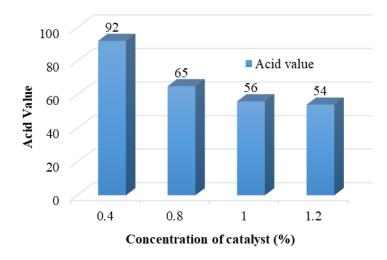

Figure 5. The effect of catalyst concentration on acid value at 200 °C, reaction time of 180 min and oleic acid / urea molar ratio of 1:4

Mechanism and kinetic of reaction

Urea has a weakly basic chemical nature [14] and it can be act as a proton acceptor in the presence of acid. Hence, the interaction between urea and oleic acid leads to formation a cation as figure 6, in which oleic acid is protonated one of the amide nitrogens of urea [15]. In next step, the NH_2 groups of intermediate compounds is transferred to $RCOO^-$ anion and CO_2, NH_3 and oleamide are formed.

Consequently, it seems that synthesis of oleamide from oleic acid and urea take place in two steps. The possible mechanism is shown in figure 6.
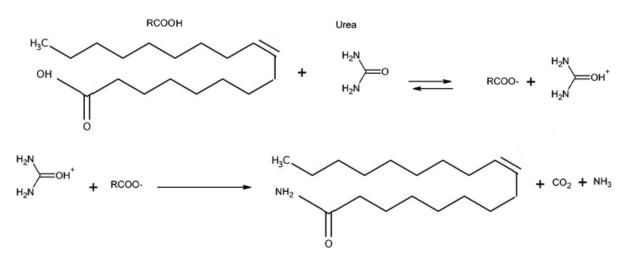
Figure 6. Proposed mechanism of oleamide synthesis

The reaction kinetics was investigated to obtain the reaction rate constant. The reaction rate can be expressed as:

$$r_{oleic\,acid} = -\frac{d\,[oleic\,acid]}{dt} = k\,[oleic\,acid][urea] \qquad (4)$$

Since, there is excess amount of urea in reaction with oleic acid / urea molar ratio of 1:4, the concentration of urea was supposed to be constant and the reaction rate was assumed to be pseudo-first-order kinetic as:

$$r_{oleic\,acid} = -\frac{d\,[oleic\,acid]}{dt} = k\,[oleic\,acid] \qquad (5)$$

$$\frac{d\,[oleic\,acid]}{[oleic\,acid]} = -k\,dt \qquad (6)$$

$$\log[oleic\,acid] = -kt + \log[oleic\,acid]_0 \qquad (7)$$

where $r_{oleic\,acid}$ is the reaction rate, $C_{oleic\,acid}$ and $C_{oleic\,acid\,0}$ represent the concentration of oleic acid before the reaction and at the time of t, respectively. The diagram of log [oleic acid] versus time (t) is shown in figure 7 in which the reaction rate constant (k) can be calculated from the slope of the linear plot. As a result, the average rate constant was calculated to be 0.0054 min^{-1} with correlative coefficient (R^2) of 0.99 for linear plot confirmed a pseudo-first-order kinetic for the reaction.
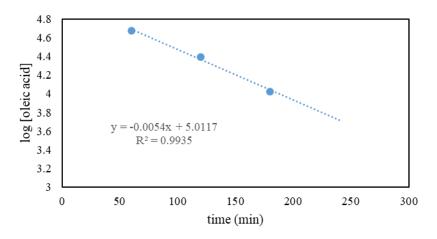
Figure 7. The plot of log[oleic acid] versus time

Conclusion

Oleamide was prepared by ammonolysis of oleic acid in the presence of urea instead of ammonia gas and $AlCl_3$ catalyst. The use of urea allowed the reaction to take place at atmospheric pressure and the presence of catalyst shortened the reaction time in which reduce the cost of synthesized oleamide. The chemical structure of synthesized oleamide was confirmed by FTIR analysis. The effect of molar ratio of oleic acid / urea, catalyst concentration, reaction temperature and time on the acid value and conversion of reaction were investigated. The optimum condition for oleamide synthesis was obtained to be oleic acid / urea molar ratio of 1:4, temperature of 200 °C, reaction time of 180 min and catalyst concentration of 1 wt%. Also, it was found that the rate of reaction is followed the pseudo-first-order kinetic. As a final result, this process with desirable operating condition could be considered as promising method for industrial preparation of oleamide.

Acknowledgement

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