VAPOUR PHASE SYNTHESIS OF ALKYLPYRAZINES USED AS FLAVOURING PRODUCTS

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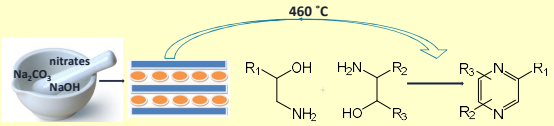
Introduction

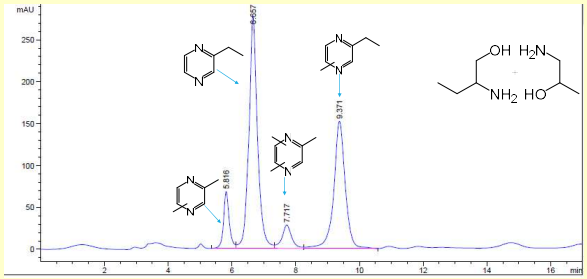
Alkylpyrazines, a class of N-heterocyclic substances, are found in many natural and synthetic compounds and therefore they have numerous applications e.g. in the food industry, as synthetic flavours. They can be used alone or in mixture and depending on the composition of the mixture the flavour may range from cocoa to baked potato flavor. Therefore, the purpose of this work was to obtain mixtures of alkylpyrazines by reacting different α-hydroxyamines, the reactions taking place in two steps, condensation and dehydrogenation. The syntheses are carried out in vapour phase, on a bifunctional ZnAl mixed oxide catalyst obtained through the calcination of the corresponding layered double hydroxide (LDH) manufactured by a mecanochemical method.

Results and discussions

The reaction pathway for the synthesis of alkylpyrazines

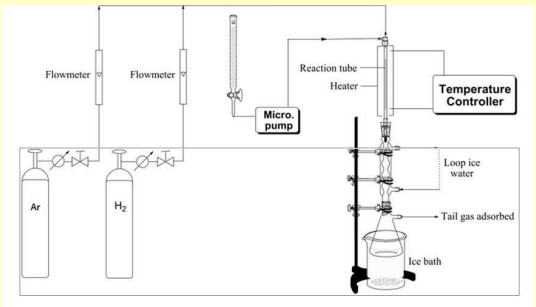


HPLC analysis of the products obtained from one of the reactions



HPLC Agilent 1200 series chromatograph at 40 °C using H_2O/ACN 30/70 (vol.) mobile phase on a Zorbax SB-C18 column (250 x 4.6 mm) at flow rate of 0.6 mL·min^{-1}

Reaction system for the synthesis of alkylpyrazines

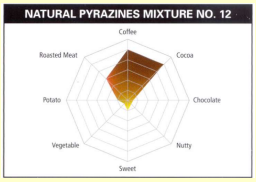


Catalyst activation: 400 °C, gas mixture Ar:H_2 = 1:1 (vol.), gas flow rate = 20 mL/min, t = 2 h
Reaction: 400 °C, reactant mixture 50% water (vol.), reactant flow rate = 1 mL/h, Ar flow rate = 10 mL/min

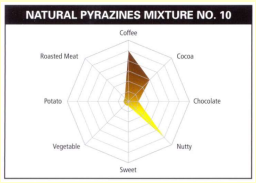
The reactions performed and the selectivities for the obtained products

Hydroxyamines							
	61.2%	19.5%	19.3%	-	-	-	-
	-	2.6%	92.4%	1.6%	-	3.4%	-
	-	7.4%	92.6%	-	-	-	-
	18.6%	52.3%	23.4%	3.8%	1.9%	-	-
	2.2%	4.6%	-	24.5%	6.4%	49.7%	12.6%
	-	6.9%	-	36.7%	16.7%	23.5%	16.2%
	-	8.8%	49.3%	6.1%	35.8%	-	-
	-	4.6%	43.3%	4.8%	38.4%	8.9%	-

Flavour of different pyrazine mixtures influenced by their composition*

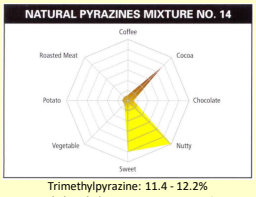


Dimethylpyrazine: 19.2 - 21.6%
Trimethylpyrazine: 13.6 - 17.3%
Ethylmethylpyrazine: 57.7 - 65.8%
Cocoa, coffee with a rosted meat undertone



Dimethylpyrazine: 5.1 - 6.8%
Trimethylpyrazine: 8.5 - 10.5%
Ethylmethylpyrazine: 30.5 - 39%
Ethyldimethylpyrazine: 33.8 - 42.1%
A mixture of cocoa, coffee and nutty nuances

Dimethylpyrazine: 69.8 - 79%
Trimethylpyrazine: 3.6 - 5.1%
Ethylmethylpyrazine: 16.2 - 22.8%
Roasted nut, can be used in nut and cocoa flavours



Trimethylpyrazine: 11.4 - 12.2%
Ethylmethylpyrazine: 19.2 - 23.4%
Ethyldimethylpyrazine: 59.3 - 66.6%
Nutty with sweet cocoa notes

* the flavour mixtures presented above were purchased from Axxence Slovakia s.r.o

Conclusions

The results obtained show that the α-hydroxyamines substituted with a methyl radical are reacting towards a single main product, with selectivities up to 92%, while those substituted with ethyl radical lead to a complex mixture of alkylpyrazines that are resembling flavour mixtures found commercially. When reacting aminobutanol with aminopropanol, the main product was obtained from the condensation of 2 aminopropanol molecules, suggesting that larger α-hydroxyamines are giving a wider variety of alkylpyrazines. The reaction is significantly influenced by the nature of the reactant, allowing to control the distribution of the end-products and the flavour of the obtained alkylpyrazine mixture.

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