THERMAL DECOMPOSITION OF TOBACCO/GLYCEROL/SBA-15 MIXTURES IN NITROGEN AND AIR ATMOSPHERES

A. Marcilla*, M.I. Beltran*, A. Gómez-Siurana*, D. Berenguer* and I. Martínez-Castellanos*

* Departamento Ingeniería Química, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain

ABSTRACT

In this work, the effect of a SBA-15 mesoporous catalyst on the qualitative composition of the gases evolved in the pyrolysis of tobacco and tobacco-glycerol mixtures is studied by TGA/FTIR, under N_2 and air atmospheres. The results obtained suggest that:

- In inert atmosphere, the addition of SBA-15 does not change noticeably the temperature of maximum decomposition rate of the main decomposition events. Nevertheless, the relative weight loss involved in the reaction steps seems to decrease.
- In oxidizing atmosphere, noticeable modifications in the thermal processes studied can be observed: the catalyst decreases the relative weight loss involved in most of decomposition steps of tobacco, and also shifts these oxidizing processes to higher temperatures. Moreover, the presence of glycerol strongly modifies the behavior of the samples, specially the last steps of the oxidation of the residues.

INTRODUCTION

Glycerol is widely used as a cigarette ingredient, acting as a moisturizing and surface active agent for flavor application, and it is generally recognized as safe [1].

In a previous work [2] the evolution with temperature of the qualitative composition of the gases evolved in the pyrolysis of glycerol, tobacco and tobacco–glycerol mixtures was reported, and the pathways for different groups of compounds and/or functional groups were shown.

Mesoporous materials, as MCM-41 and SBA-15 appear as interesting materials because their ability for reducing the cigarettes smoke toxicity. Thus, the knowledge of the influence of these catalyst on the pyrolytic behaviour of tobacco, additives and tobacco-additives mixtures could be an interesting issue.

METODOLOGY

Materials: 3R4F cigarettes from the Reference Cigarette Program of the University of Kentucky and glycerol (CAS number 56-81-5, purity >99.0%) provided by Sigma-Aldrich were used. The mixtures were prepared with around 15% SBA-15 (w/w) and 25% glycerol (w/w).

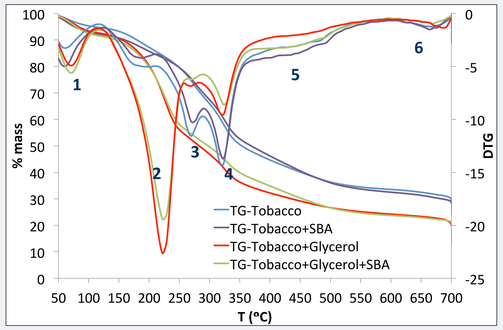
Experimental equipment: TGA Metller Toledo thermobalance at heating rate of 35 ºC/min under a gas (N_2 or air) flow of 80 mL·min^{-1} (STP) connected to a Bruker Tensor 27 FTIR spectrometer through a heated line (200 ºC).

Catalyst: SBA-15 prepared in our laboratory [3] with pore size = 6,09 nm, BET area =757 m^2/g and total volume of pores = 1,06 cm^3/g.

Thermogravimetric analysis in N_2 atmosphere

PROCESSES OBSERVED

1. Loss of moisture
2. Evaporation of glycerol and others volatiles
3. Pyrolysis of hemicellulose, pectine etc.
4. Pyrolysis of cellulose and others
5. Pyrolysis of lignin and residue from previous steps
6. Pyrolysis of char and inorganic compounds



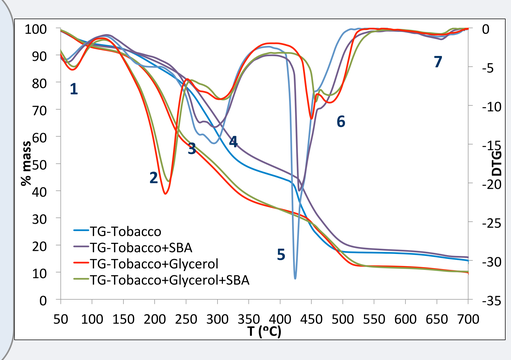
% mass normalyzed as follows:
100 x total mass/[total mass – dry SBA-15 mass]

- In N_2 atmosphere the temperature of decomposition steps is not significantly affected by SBA-15
- Oxygen clearly modifies the behaviour of thermal processes
- In air atmosphere the peaks at around 260 and 320 ºC appear at lower temperatures
- SBA-15 decreases the intensity of all peaks
- SBA-15 shifts the oxidizing processes to higher temperatures

Thermogravimetric analysis in air atmosphere

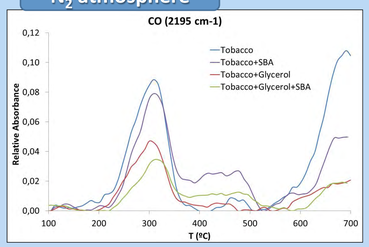
PROCESSES OBSERVED

1. Loss of moisture
2. Evaporation of glycerol and others volatiles
3. Decomposition of hemicellulose, pectine, etc.
4. Decomposition of cellulose and others
5. Combustion of remaining materials
6. Combustion of light coke, char and inorganic compounds
7. Decomposition of hard coke

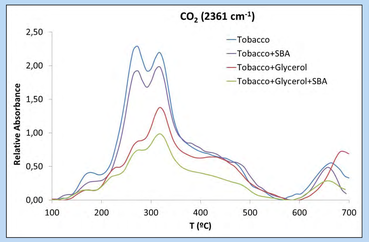


Evolution with the temperature of the relative absorbance (i.e.: absorbance at T divided by the area under the GS curve/(mass of tobacco or mass of tobacco+glycerol) of selected bands

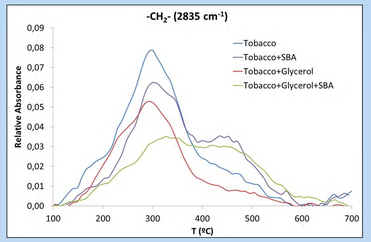
N_2 atmosphere



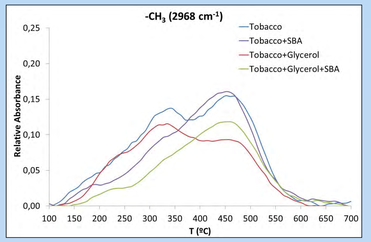
Important reduction of CO in the presence of catalyst, but slight increase around 450ºC in the case of the mixture.



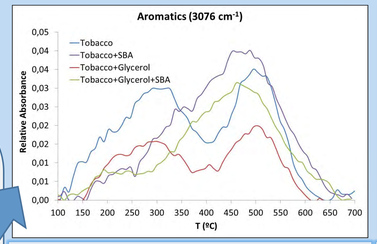
Important reduction of the yields of CO_2 in the presence of SBA-15.



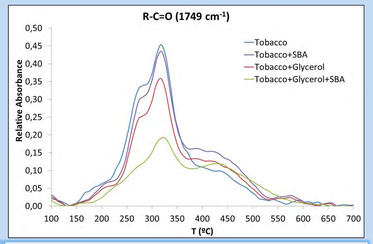
SBA-15 provokes a decrease of the yields at low temperature and an important increase at around 450ºC.



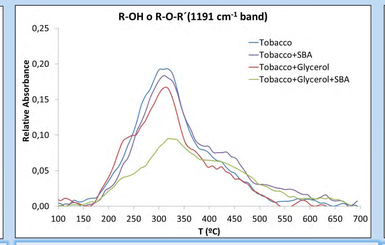
In the presence of SBA-15 a decrease of the yields at low temperatures and an increase at hight temperatures occur.



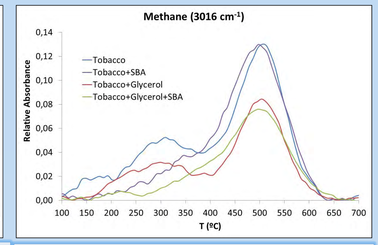
Important decrease in the first step and increase at higher temperatures in the presence of SBA-15.



Important effect of the catalyst when glycerol was added to tobacco.

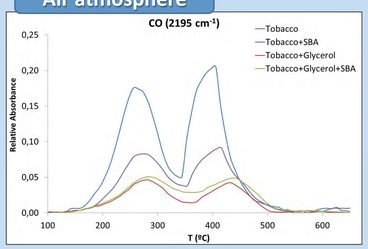


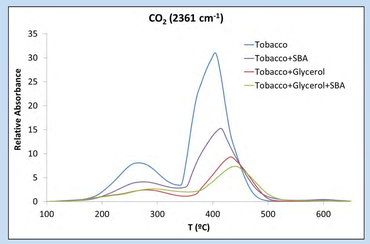
Important effect of the catalyst when glycerol was added to tobacco.

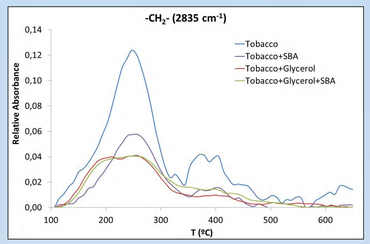


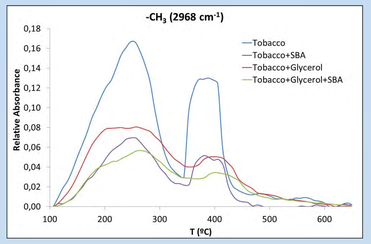
At low temperatures SBA-15 provokes a noticeable reduction of CH_4. At higher temperatures the decrease is not significant.

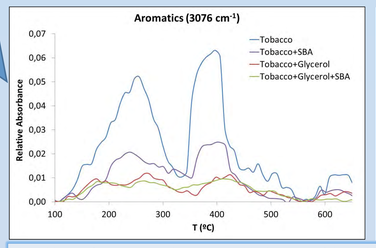
Air atmosphere

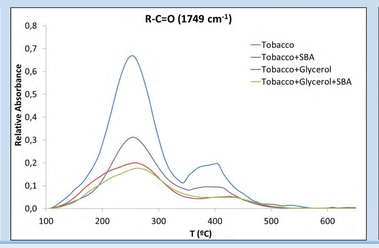


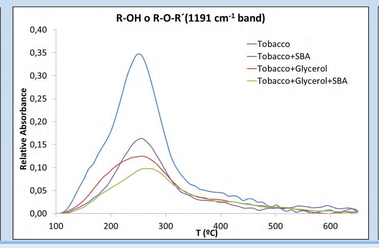


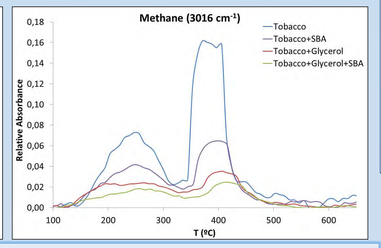












The addition of SBA-15 provokes a noticeable decrease of the yields from tobacco for all the functional groups studied in this work. However, the effect on the glycerol-tobacco mixture is very low or negligible.

FTIR spectra (N_2)

Tobacco | Tobacco+SBA | Tobacco+Glycerol | Tobacco+Glycerol+SBA

FTIR spectra (air)

Tobacco | Tobacco+SBA | Tobacco+Glycerol | Tobacco+Glycerol+SBA

CONCLUSIONS

- The addition of SBA-15 practically does not change the temperature of the decomposition in N_2 atmosphere, but produces clear modifications in air atmosphere.
- The presence of the catalyst decreases the intensity of all the decomposition steps observed in TG (in N_2 and air atmospheres), with the only exception of the stage related to the shoulder at the highest temperatures in the air atmosphere.
- The presence of glycerol strongly modifies the behavior of the samples, specially the last steps of the oxidation of the residues (TG in air).
- Water, carbonyl and hydroxyl compounds, CO and CO_2 seem to be mainly formed (in N_2 atmosphere) in the lower temperature decomposition steps.
- At higher temperatures (at around 500 ºC in N_2 atmosphere), an increase of methane, aromatics, and $–CH_3$ is observed in N_2 atmosphere.
- SBA-15 produces a decrease in the formation of all the studied functional groups in the range of 200-300 ºC, but increases the formation of aromatics at around 500ºC (in N_2 atmosphere).
- In air atmosphere two types of processes can be observed, one at around 250-300 ºC, similar to that in N_2 atmosphere and thus attributed to pyrolysis, and another at around 400ºC, attributed to oxidation or combustion processes.
- The yields of CO, $-CH_3$ groups and aromatic compounds obtained in air atmosphere seem to be relatively similar in the pyrolysis and the oxidation processes, whereas the yields of CO_2 and methane increase noticeably in the processes at higher temperatures, and $-CH_2-$ groups and alcohols and/or ethers at lower temperatures.
- The generation of alcohols and ethers seems to be only associated with the step at around 250 ºC
- In air atmosphere, the addition of SBA-15 provokes a noticeably decrease of all the functional groups studied, specially in the case were no extra glycerol was added, thus confirming the utility of this material as a reducer of the toxicity of tobacco smoke

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REFERENCES

[1] E.L. Carmines, C.L. Gaworski, Food Chem. Toxicol., 43 (2005), p. 1521.

[2] A. Gómez-Siurana, A. Marcilla, M. Beltrán, D. Berenguer, I. Martínez-Castellanos, S. Menargues, Thermochim. Acta, 573 (2013), p. 146.

[3] Marcilla, A.; Beltrán, I.; Gómez, A.; Navarro, R.; Berenguer, D.; Martínez, I., Aluminosilicato SAB-15 como aditivo para la reducción de los compuestos tóxicos y cancerígenos presentes en el humo del tabaco, P201201266, Spain 2012.