EuroBioRef

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SP5 – <Advanced Catalytic Conversion Processes to Chemicals and Integrated Separation Technologies>
WP5.2 – <Acetals Production>

Deliverable report

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Approval				
	Name	**Organization**	**Date**	**Visa**
Deliverable Responsible	Jean-Luc COUTURIER	Arkema	21/01/2013	OK
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Dissemination level		
PU	Public	X
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Content

Executive summary

Description of the deliverable objective and content

PolyOxyMethylenedialkylethers, made out of methanol or ethanol and formaldehyde, are known as possible substitutes for diesel fuels and some of them as a methanol substitute in direct methanol fuel cells. These molecules have shown a low toxicity. The objective of Arkema was to optimize the process and to try to formulate a new blend suitable for aviation fuels. 1 kg samples were targeted for application tests by OBRPR in WP7.4.

Brief description of the state of the art

POMM (PolyOxyMethylene-diMethylether) synthesis is known for a long time. It consists in the reaction of methylal with formaldehyde or paraformaldehyde or trioxane in the presence of an acid catalyst. We can mention the Du Pont patent in 1948 (US2449469 – catalyst sulphuric acid) or the Mitsui patent in 1972 (FR2119600 – catalyst acid resin).
Patents from BP (WO0029364, WO0029365 in 2000) claimed processes from methanol or dimethylether or ethanol with different catalysts (acid resins, zeolites, Cu, Ag, Zn, Mo) and claimed the resulting composition as fuel.
Snamprogetti has two patents concerning the use of 1-20% POM in fuel (EP1070755 in 2001) and the substitution of diesel by pure POM (EP1422285 in 2004).
Some more recent patents from BASF claimed a process with low water content (EP1809590 in 2007) and a fuel mixture comprising POM (EP2104726 in 2009).
The goal of EuroBioRef was to look for a specific formulation for aviation fuel to circumvent these patents.

Deviation from objectives and corrective actions

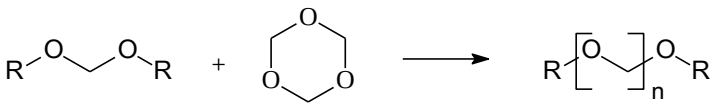
There is no deviation with respect to the DoW. Samples of POM have been prepared and evaluated by OBRPR for aviation fuel but results are disappointing. In consequence, we have also worked on formulations for a niche application which is formaldehyde substitution in embalming.

Innovation brought and technological progress

The POM process studied in the project has been shown to be robust enough to prepare samples and scale up would be easily possible in multipurpose pilot plants. Main innovation should come from the aviation fuel application but the products failed at the preliminary evaluations tests.

Analysis of the results

We have studied the POMM ($R=CH_3$) and POME ($R=C_2H_5$) synthesis. The synthesis is made by reaction of methylal or ethylal with trioxane in the presence of an acid catalyst:

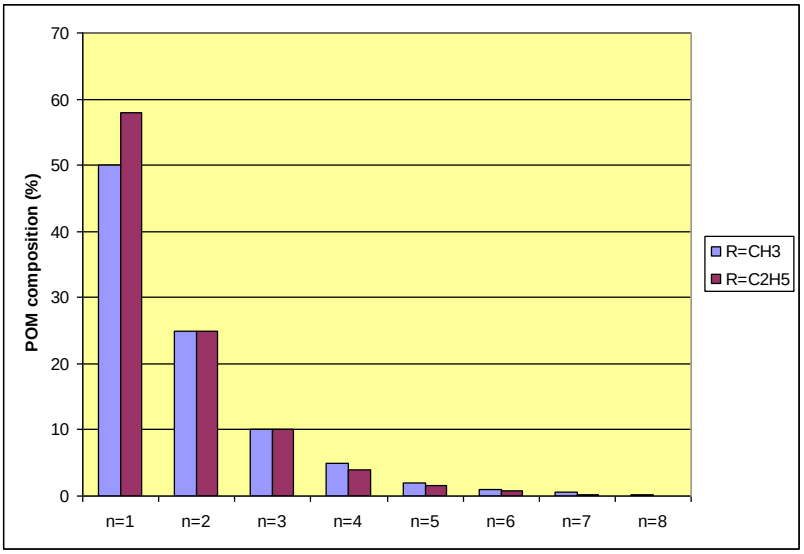


$R=CH_3, C_2H_5$

The reaction gives an equilibrium mixture of $R-(OCH_2)_n-OR$ with n=1-8.

We have done a screening of acid catalysts using a neat batch process. Several catalysts have allowed reaching the equilibrium at 40°C (sulphuric acid, triflic acid, $BF_3.OEt_2$, Amberlyst resins 15 and A36) whereas some catalysts are inactive (phosphoric acid, phosphoric acid on silica, boric acid). The acid resin catalyst Amberlyst 15 has been selected as it gives the equilibrium in 15 minutes and as they can easily be removed from the reaction mixture by filtration. The optimum temperature for the reaction is 30-50°C and we have shown that water inhibits the reaction.

The equilibrium mixture is somewhat different in case of POMM and POME:



The separation process has been studied. In the case of POMM, We have shown that we can recover POMM-2 (n=2) or POMM-3 (n=2) as pure products or we can get POMM-2,8 (n=2-8) or POMM-3,8 (n=3-8) cuts. We have selected the POMM-2,8 cut that was a good compromise between yield and acceptable flammability. In the case of POME, we have isolated a POME-3,8 (n=3-8) cut to compare in the aviation fuel application a higher boiling point product.

Samples prepared

Two samples have been prepared as planned in the DoW:

Sample	Composition	Quantity (L)	Boiling point (°C)	Solubility in water (%)
N°1	POMM-2,8	1	>105°C	≈30%
N°2	POME-3,8	0.5	>185°C	<5%

These two samples have been provided to OBRPR for aviation fuel evaluation.

Impact of the results

The POMM and POME process is validated and could be easily scaled up at pilot scale as initially planned in the DoW in tasks 7.3.3 (optimization and scale up) and T8.3.2 (demo). Unfortunately the products failed in the preliminary aviation fuel evaluations. In consequence, these tasks have been put on hold to focus on more promising products in the project. Other fuel applications (road fuel, fuel cells) or niche application (embalming) would have to be investigated to justify to move to the demo phase.

Related IPR

No new results have been considered patentable. The process is in the public domain and results are negative in aviation fuel.

Publishable information

No publication planned

Conclusion

The POMM and POME process is set up at lab scale and **two samples have been prepared as planned in the DoW: 1 L of POMM-2,8 and 0,5 L of POME-3,8**.

The samples have been evaluated for aviation fuel by OBRPR. They have been tested as components used at several % in conventional aviation fuel. The two candidates failed. The products are not compatible with conventional aviation fuel (especially not soluble at low temperature) and there is a water reaction issue in the sense that the products are too soluble in water. We were far from the target expected by OBRPR.

The process could have been easily moved to the scale up (SP7) and demo (SP8) phases but there is an application issue. Whatever the formulation, it is unlikely to reach all the aviation fuel requirements with POM. Apart from the compatibility and water reaction issues, there would be also an energy density issue due to the high oxygen content of POM.

Back up solutions would be to promote the products in other fuel applications such as road fuels (existing patents from BP, Snamprogetti and BASF) or fuel cells (existing patents from Arkema). Embalming is also a promising niche application where POM could substitute carcinogen formaldehyde. Arkema is currently investigating this application with POMM-2,8. These applications could be developed in the future through the interest group.

POM process description

✓ **Experimental protocol** (POMM)

In a double-jacket glass reactor, we introduce 76.1g of methylal (1 mol), 22.5g of trioxane (0.75 mol of CH_2O) and 3.8g of Amberlyst 15. We heat at 40°C under stirring during 15 minutes. The trioxane conversion is >95%. The reaction mixture is filtrated and washed with a caustic soda solution at 15%. The product is analyzed by GC. The POMM-2,8 cut can be recovered from the reaction mixture by evaporation under vacuum of unconverted methylal.

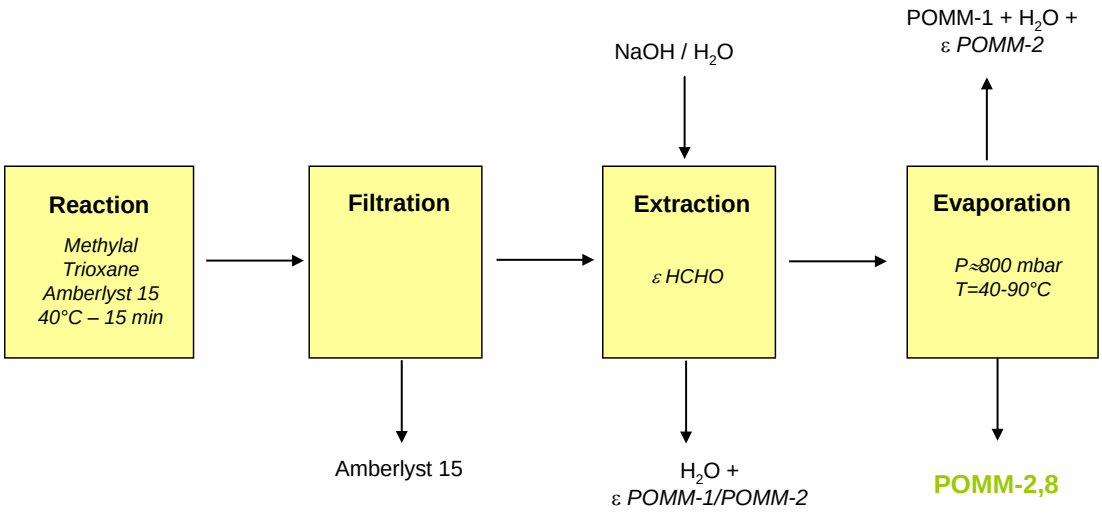
✓ **Catalysts screening**

Different catalysts (homogeneous or heterogeneous) have been tested in the POMM synthesis:

Catalyst	Amount (%)	T (h)	POMM-n (GC surface %)						
			n=1	n=2	n=3	n=4	n=5	n=6	n=7
H_2SO_4	10	2	54	26	10	4	2	0.9	0.4
	5	8	56	25	11	4	1.4	0.4	0
H_3PO_4	10	5	85	0.3	0	0	0	0	0
H_3BO_3	10	6	90	0	0	0	0	0	0
CF_3SO_3H	10	0.25	53	25	11	5	2	0.9	0.4
	10	2	52	25	11	5	2	0.9	0.4
$BF_3.OEt_2$	10	6	53	26	12	5	2	1	0
Amberlyst 15	5	0.25	47	29	13	5	2	0.7	0.2
	5	1	47	29	14	6	2	0.9	0.3
Amberlyst A36	5	0.25	54	26	11	5	2	0.9	0.4
	5	1	52	27	13	5	2	1	0
H_3PO_4/SiO_2	5	6	90	0	0	0	0	0	0

The Amberlyst 15 catalyst has been selected for the samples preparation.

✓ **Process scheme** (POMM-2,8)



Samples analysis

Samples provided to OBRPR:

Sample N°1 : POMM-2,8 Composition $CH_3(OCH_2)_nOCH_3$	% (GC surface)
n=2	48.6
n=3	32.9
n=4	12.0
n=5	3.8
n=6	1.3
n=7	0.5
n=8	0.1
n=1	*0.3*

Sample N°2 : POME-3,8 Composition $C_2H_5(OCH_2)_nOC_2H_5$	% (GC surface)
n=3	47.8
n=4	30.0
n=5	13.0
n=6	5.4
n=7	2.2
n=8	0.9
n=2	*0.5*