



## Cross-Coupling of Bio-oxygenates over Heterogeneous Catalysts

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The importance of synthesis of carbon-carbon bonds is reflected by the fact that Nobel Prizes in Chemistry have been given to this area: The Grignard reaction (1912), the Diels-Alder reaction (1950), the Witting reaction (1979), the olefin metathesis Y. Chauvin, R.H. Grubbs and R.R. Schrock (2005), the palladium-catalyzed cross-coupling reactions to R. F. Heck, A. Suzuki, E. Negishi.

Here, we present the new heterogeneous catalytic cross-coupling reaction of a number of bio-oxygenates that lead to expand considerably the hydrocarbons incorporating. For catalytic experiments, mono- and bimetallic Pt-M and Re-M were used. As substrates we used ethanol (the most shared bioalcohol), glycerol (co-product of biodiesel production), n-butanol, propanol and acetone (prospective bioproducts) and vegetable oil.

It was found that the main products of ethanol conversion are alkanes with even number of carbon atoms. When we used C<sub>3</sub> co-reagents (propanol, acetone, glycerol) products composition was enriched with hydrocarbons with odd number of carbon atoms. That gave us a reason to propose cross-coupling reactions take place during combined conversion of bio-oxygenates. Glycerol was found to be the best co-reagent to ethanol. Its addition (not more than 40 wt.%) to ethanol halves C<sub>1</sub>-C<sub>2</sub> yields and increases hydrocarbons yield by 20-30 wt.% in comparison with pure ethanol conversion products.

### 1. Introduction

Nowadays, a significant interest has been concentrated on effective approaches related to renewable biomass conversion to fuels (Ragauskas et. al., 2006). Ethanol, butanol, iso-propanol, n-propanol and acetone (by-product of fermentation butanol production) produced via the fermentation of biomass. Glycerol is generated in large quantities as a by-product of the triglycerides transesterification (Gude et. al., 2013). All of this bio-oxygenates can be incorporated into gasoline and biodiesel, either directly or after catalytic conversion into more effective additives.

Earlier the new catalytic reaction of alcohol conversion towards hydrocarbons of gasoline and diesel fractions was found (Tsodikov et. al., 2004). This reaction named reducing dehydration of alcohols proceeds in an inert atmosphere Eq.1. Hydrogen required for alkane formation was formed via parallel reactions of partial ethanol dehydration and/or aromatization.



In process of developing of reducing dehydration of alcohols reaction a possibility was found to carry on combined conversion of ethanol with cyclopentanol into alkyl substituted cycloalkanes (Eq.2) over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (Tsodikov et. al., 2008). Also Pt-containing catalysts showed high activity and selectivity in the reaction of ethanol conversion towards fuel hydrocarbons (Tsodikov et. al., 2014).

The importance of synthesis of carbon-carbon bonds is reflected by the fact that Nobel Prizes in Chemistry have been given to this area: The Grignard reaction (1912), the Diels-Alder reaction (1950), the Witting

reaction (1979), the olefin metathesis (Chauvin et al., 2005), the palladium-catalyzed cross-coupling reactions to R. F. Heck, A. Suzuki, E. Negishi (Astruc, 2011).



where R = C<sub>2</sub>H<sub>5</sub>; C<sub>2</sub>H<sub>3</sub>; C<sub>3</sub>H<sub>7</sub>; C<sub>4</sub>H<sub>9</sub>

Here, we present the new heterogeneous catalytic cross-coupling reaction of a number of bio-oxygenates that lead to expand considerably the hydrocarbons incorporating.

## 2. Materials and Methods

Analytical grade ethanol (96 %) was used without further purification. For catalytic experiments, industrial Pt-containing catalysts samples (Pt/Al<sub>2</sub>O<sub>3</sub>, PR-56, Pt-Re/Al<sub>2</sub>O<sub>3</sub>) were used. The cross-coupling reaction of bio-oxygenates was performed in a flow-circulation unit with a stationary catalyst layer under argon at 623 K, 5 bar, VHSV (volume hours space velocity) 0.6 h<sup>-1</sup>, and a multiplicity of gas circulation of 50 cm<sup>3</sup>/min. Qualitative and quantitative analyses of the C<sub>1</sub>–C<sub>5</sub> hydrocarbon gases were performed by gas-liquid chromatography (GLC) with a Kristall-4000M chromatograph (detector: FID, carrier gas: He, column: HP-PLOT/Al<sub>2</sub>O<sub>3</sub>, 50 m × 0.32 mm). GLC analyses of CO, CO<sub>2</sub> and H<sub>2</sub> were performed with a Kristall-4000 chromatograph (detector: TCD, carrier gas: Ar, column: SKT, 1.5 m × 4 mm). The qualitative composition of the C<sub>6</sub>+ hydrocarbons in the aqueous and organic phases were identified by gas chromatography–mass spectrometry (GC-MS) using a MSD 6973 - and an Automass-150 spectrometer - (EI = 70 eV, sample volume = 1 µl, columns: HP-5MS, 50 m × 0.32 mm and CPSil-5, 25 m × 0.15 mm). The quantitative content of the organic compounds was determined by GLC using a Varian 3600 chromatograph (detector: FID, carrier gas: He, column: Chromtec SE-30, 25 m × 0.25 mm). Trifluoromethyl benzene was used as an internal standard for the organic layer, and internal normalization was used for the aqueous layer. The ethanol content in the aqueous phase was determined by GC-MS using the absolute calibration method on the ratio of alcohol to water integral signals.

## 3. Results and Discussion

Cross-coupling of ethanol and a number of bio-oxygenates was investigated over 1.5%Re-3.5%W/Al<sub>2</sub>O<sub>3</sub> catalyst. It was found that glycerol provide the maximum increasing of C<sub>3</sub>+ hydrocarbons fraction yield, up to 57%, and that is the most suitable co-reagents for use with ethanol (Table 1).

*Table 1: Composition (wt.%) of carbon containing products of ethanol and various bio-oxygenates mixture conversion under optimal conditions over 1,5Re-3,5%W/Al<sub>2</sub>O<sub>3</sub> catalyst*

	EtOH	EtOH+20vol.%PrOH	EtOH+20 vol.%BuOH	EtOH+20 vol.%Glycerol
C1	0.1	2.2	0.1	2.0
C2	8.8	14.9	9.9	4.0
C2=	20.2	16.5	17.9	1.9
C3	0.1	0.5	0.1	0.3
C3=	0.8	1.9	1.2	7.9
C4	4.4	12.5	6.7	0.7
C4=	17.7	12.5	24.8	18.1
C5	0.8	11.0	0.2	1.2
C5=	0.2	4.5	0.3	9.3
C6	0.7	0.7	1.1	0.7
C6=	6.1	6.5	11.1	13.7
C7=	-	3.0	0.0	2.3
C8=	1.2	0.7	3.2	1.7
C9=	-	-	-	1.1
ΣC <sub>3</sub> +	31.8	53.8	48.7	56.9

Influence of glycerol concentration for products composition was investigated. As shown in Table 2 the optimal glycerol concentration for its conversion with ethanol is 20 vol.%. An excess of 20 vol.% concentration of glycerol content in feeding mixture leads to decrease yield of aim fraction (C<sub>3</sub>+ hydrocarbons), unspecified nonvolatile substances formation and catalyst coking. With further increase of the glycerol proportion in the reaction mixture the selectivity drastically changes: instead of aliphatic hydrocarbons the nondescript mixture of oxygenates are formed. Also acrolein- a product of the thermal decomposition of glycerol - polymerize to resins.

*Table 2: Composition (wt.%) of carbon containing products of ethanol and various concentration of glycerol mixture conversion under optimal conditions over 1.5%Re-3.5%W/Al<sub>2</sub>O<sub>3</sub> catalyst.*

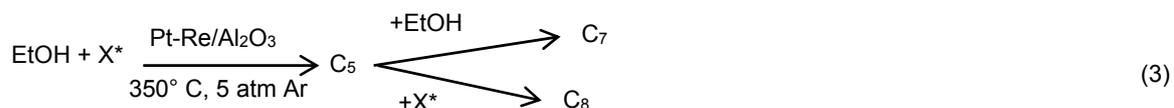
EtOH+	20 vol.% Glycerol	40 vol.%Glycerol
C1	1.95	4
C2	4.01	1.25
C2=	1.93	2.41
C3	0.25	0.25
C3=	7.9	3.1
C4	0.7	0.8
C4=	18.11	12.5
C5	1.2	-
C5=	9.26	9.2
C6	0.7	-
C6=	13.7	8.8
C7=	2.3	3.8
C8=	1.7	1.7
C9=	1.1	1.85
ΣC <sub>3</sub> +	56.9	42.0

Ethanol and glycerol mixture conversion was investigated over wide number of catalysts. As shown in Table 3 yield of hydrocarbons C<sub>3</sub>+ about the same, but glycerol contribution in cross-coupling products formation over Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalyst exceeds 60%. So It may be predicted that Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalyst is the most prospective for further investigations of cross-coupling process over heterogeneous catalysts.

*Table 3: Ethanol and glycerol mixture conversion under optimal conditions over wide number of catalysts*

catalyst	Yield C <sub>3</sub> +, wt.%	% glycerol in C <sub>3</sub>	% glycerol cross
Pt-Re/Al <sub>2</sub> O <sub>3</sub>	53.2	31.5	62.2
1,5Re-3,5%W/Al <sub>2</sub> O <sub>3</sub>	49.8	3.8	24.2
Ta-Re/Al <sub>2</sub> O <sub>3</sub>	57.4	16.6	28.4
Ga/Al <sub>2</sub> O <sub>3</sub>	57.1	23.8	29.1
Cu/Al <sub>2</sub> O <sub>3</sub>	60.1	8.0	23.8
0,1Au-0,003Ni/Al <sub>2</sub> O <sub>3</sub>	61.3	21.2	28.2

To test Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalyst selectivity in cross-coupling reaction it was carried out combine ethanol with different alcohols conversion. The criterion of reaction efficiency was the ratio of primary products according to Eq. 3 yield to ones obtained via pure ethanol conversion.



\* - X substrate C<sub>3</sub> (propanol, acetone, glycerol, propene)

Data of catalytic experiments shows that cross-coupling products yield increases in 1-3 orders depending on co-reagent (Table 4). The highest efficiency was observed for C<sub>5</sub> formation and decreased from C<sub>7</sub> to C<sub>8</sub>. The reason of low ratio C<sub>8</sub>/C<sub>8</sub> EtOH may be explained with ethanol can form C<sub>8</sub> by itself. Acetone was found to be the most active co-reagent with ethanol. Primary cross-coupling products yield was maximum during acetone and ethanol conversion.

*Table 4: Mole ratio of the yield of primary cross-coupling products obtained via combined conversion of bio-oxygenates with ethanol to yield of ones obtained via ethanol conversion over Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalyst*

	C <sub>5</sub> /C <sub>5</sub> EtOH	C <sub>7</sub> /C <sub>7</sub> EtOH	C <sub>8</sub> /C <sub>8</sub> EtOH
EtOH+nPrOH (40%)	697	94	12
EtOH+iPrOH (50%)	141	35	2
EtOH+Acetone(40%)	1166	429	43
EtOH+Glycerol (20%)	616	177	21

*Table 5: Composition (wt.%) of carbon containing products of ethanol and various concentration of acetone mixture conversion under optimal conditions over Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalyst*

Conversion products	Acetone vol.%					
	100	50	40	20	10	0
C <sub>1</sub>	1.2	6.5	2	7.9	8.6	7.7
C <sub>2</sub>	1	6.9	3.3	21.1	25.9	31.2
C <sub>3</sub>	11.3	18.2	8.4	13.3	12.5	6.6
C <sub>4</sub>	6.8	11.2	5.6	8.3	10.2	20.7
C <sub>5</sub>	8.1	11.8	13.5	7.8	4.4	3.9
C <sub>6</sub>	-	-	1.1	2.5	2.9	8
C <sub>7</sub>	-	-	16.3	5.5	3.9	1.6
C <sub>8</sub>	-	-	5.7	4.1	1.7	1.9
C <sub>9</sub>	-	-	0.3	2.6	3	0.6
C <sub>10</sub>	-	-	-	1.4	0.6	0.3
C <sub>11</sub>	-	-	-	1.3	0.8	0.1
C <sub>12</sub>	-	-	-	0.7	0.7	-
ΣC <sub>3+</sub>	26.1	41.2	51	47.3	40.6	43.7
aromatics	57.5	17	21.7	2.7	3.2	0.9
oxygenates	8.8	13.3	15.6	3.1	1.2	0.4
CO	0.1	1.7	1.8	4	5.2	3.7
CO <sub>2</sub>	5.3	13.4	4.5	13.9	15.1	12.3

To determine co-reagent concentration influence on products yield was used acetone. The results of co-reagent concentration influence are presented in Table 5. Conversion of pure acetone mainly leads to propane and aromatics formation. As the reaction was carried out in inert atmosphere of Ar. hydrogen that is necessary for alkanes formation was formed during the reaction via parallel reaction of intermediates including aromatization. As acetone concentration decreased in feed aromatics content in products also decreased down to 3.2 wt.% at 10 vol.% acetone in feed. Optimal acetone concentration was found to be 40 vol.% that

provides the maximum yield of alkanes  $C_{4+}$  equal to  $\approx 40$  wt.% and 20 wt.% of aromatics. So the total amount of fuel hydrocarbons reached up to 60 wt.%.

Composition of hydrocarbons  $C_{4+}$  obtained during ethanol with different co-reagents conversion is shown in figure 1. Depending on the nature of the co-reagent the aim fraction ( $C_{3+}$  hydrocarbons) may consist of different hydrocarbon classes: alkanes, olefins, aromatics. Concentration of alkanes correlates with concentration of aromatics – the more alkanes obtained the more aromatics formed. In consequence of aromatics products forming hydrogen is produced that consumed in the formation of alkanes from initial alcohol. Over Pt-Re catalyst the most probable source of hydrogen is aromatics according to Eq.4

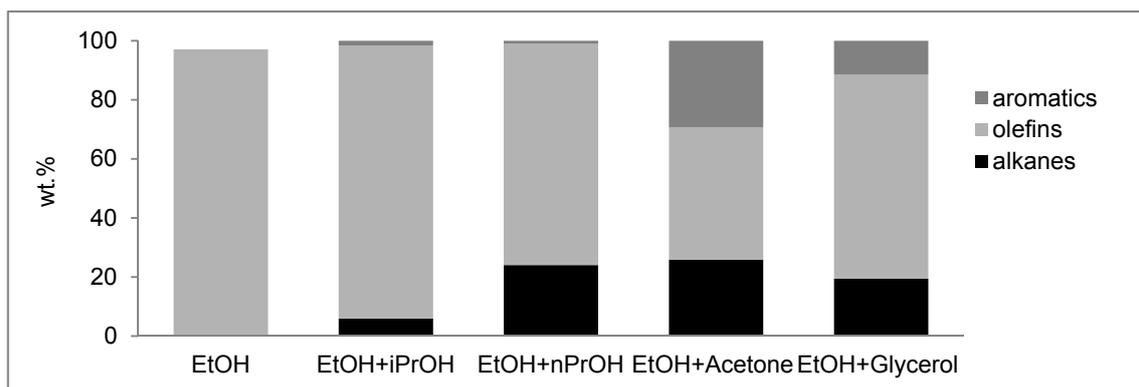


Figure 1: Composition (wt.%) of hydrocarbons  $C_{4+}$ ,  $T=350^\circ\text{C}$ , 5 atm Ar, over Pt-Re/ $\text{Al}_2\text{O}_3$  catalyst

Earlier was found that during fatty acids triglycerides conversion over Pt/ $\text{Al}_2\text{O}_3$  catalyst glycerol fragment take part in hydrocarbon chain growth forming alkanes with a number of carbon atoms exceeds the one in initial fatty acids. To check the phenomenon we converted the simplest ester – ethyl acetate. During its conversion products up to  $C_9$  were found as shown in Figure 2, that confirms the possibility of intermolecular cross-coupling of esters. The main product was  $C_6$  olefins fraction. The presence of hydrocarbons with odd number of carbon atoms in its hydrocarbon skeleton testifies that  $C_2$  and  $C_1$  fragments formed during hydrogenation of C-O bonds and decarboxylation respectively may interact.

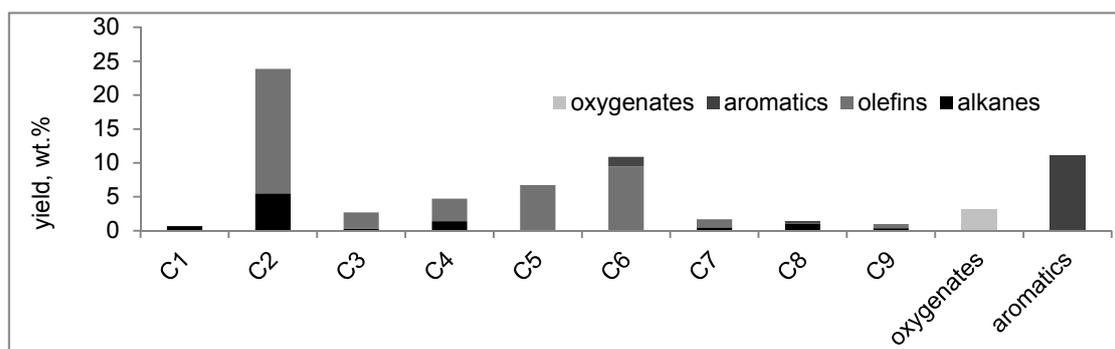


Figure 2: Ethyl acetate conversion products,  $T=420^\circ\text{C}$ , 5 atm Ar over Pt-Re/ $\text{Al}_2\text{O}_3$  catalyst

Investigations of Butylmethacrylate conversion over Pt-Re/ $\text{Al}_2\text{O}_3$  catalyst under conditions similar to rapeseed oil conversion showed that Butylmethacrylate could be incorporated in mainly  $C_3$ - $C_4$  fraction but also  $C_5$ - $C_7$  fraction was obtained. Hydrocarbons  $C_5$ - $C_7$  yield was 14 wt.% that is lower than in example with ethyl acetate. This phenomenon may be explained that hydrogen interrupts carbon chain growth. As a result in hydrogen atmosphere it is possible to obtain lower quantity of cross-coupling products and hydrocarbons will contain lower number of carbon atoms than in inert atmosphere.

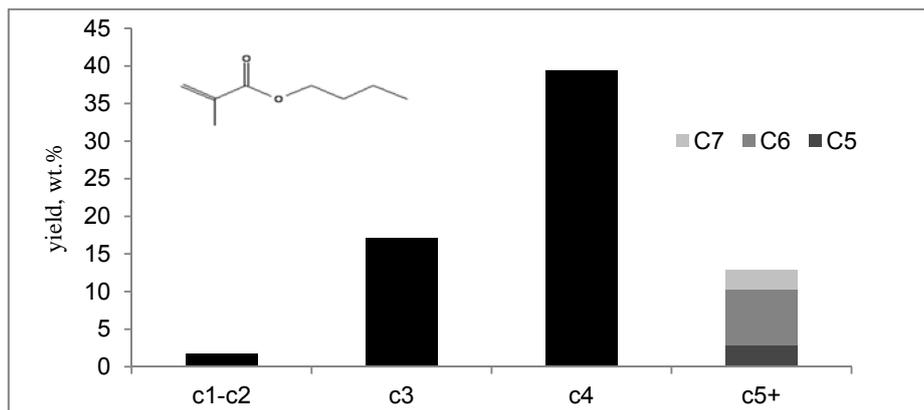


Figure 3: Butylmethacrylate conversion products,  $T=330^{\circ}\text{C}$ , 50 atm  $\text{H}_2$ , 0,6  $\text{h}^{-1}$  over Pt-Re/ $\text{Al}_2\text{O}_3$  catalyst

#### 4. Conclusions

Acetone and glycerol were found to be the most prospective co-reagents with ethanol. Its addition increase the aim fraction yield of hydrocarbons  $\text{C}_4\text{-C}_{12}$  up to 60 wt.%. Analysis of ethanol conversion products showed that among its hydrocarbons with even number of carbon atoms dominates. Addition of glycerol, acetone and propanol to ethanol leads to increasing of hydrocarbons with odd number of carbon atoms yield. Comparison of primary cross-coupling products (hydrocarbons  $\text{C}_5$ ,  $\text{C}_7$ ,  $\text{C}_8$ ) obtained via ethanol conversion and combined conversion of ethanol with  $\text{C}_3$  substrate (propanol, glycerol, acetone) showed that its yield increased by 100-1000 times.

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