Supplementary Data and Information – Oxidative Methylation of Aromatics over Zeolite Catalysts

Table SD1 – Data for calculating AE, CE, RME, EMY, MI and MP

Reaction	Catalyst/Amount of catalyst (g)	Reagent	Mol. weight of Reagent (g/mol)	Moles of Reagent converted	Amount of Reagent converted (g)	Mol. weight of Toluene product (g/mol)	Amount of Toluene product (g)
Equation 14	HZSM-5/0.2	Benzene	78.11	9.378×10^{-4}	0.07327	92.14	0.1018
		Methanol	32.04	1.579×10^{-3}	0.05061		
	CoZSM-5/0.2	Benzene	78.11	9.823×10^{-4}	0.07674	92.14	0.1015
		Methanol	32.04	1.609×10^{-3}	0.05156		
	CuZSM-5/0.2	Benzene	78.11	9.844×10^{-4}	0.07691	92.14	0.1044
		Methanol	32.04	1.607×10^{-3}	0.05149		
Equation 15	HZSM-5/0.055	Benzene	78.11	2.181×10^{-4}	0.01704	92.14	0.01869
	0.31 % O_2 used	Methane	16.043	2.181×10^{-4}	0.003499		
		Oxygen	32.0	1.090×10^{-4}	0.003489		
		Benzene	78.11	5.282×10^{-4}	0.04126	92.14	0.04118
	1.42% O_2 used	Methane	16.043	5.282×10^{-4}	0.008474		
		Oxygen	32.0	2.641×10^{-4}	0.008452		

Table SD2 – Data for calculating RMC

Reaction	Catalyst	Reagent	Mol. weight of Reagent (g/mol)	Liquid Density (g/ml) or Gas Specific Vol. (m^3/kg)	Reagent cost* ($AUS/kg)	Toluene yield (%)	Mol. weight (g/mol)/Mass of Toluene produced (g)
Equation 14	HZSM-5	Benzene	78.11	0.874	33.75	22.12	92.14/0.1018
		Methanol	32.04	0.791	8.38		
	CoZSM-5	Benzene	78.11	0.874	33.75	24.13	92.14/0.1015
		Methanol	32.04	0.791	8.38		
	CuZSM-5	Benzene	78.11	0.874	33.75	24.88	92.14/0.1044
		Methanol	32.04	0.791	8.38		
Equation 15	HZSM-5	Benzene	78.11	0.874	33.75	3.88	92.14/0.01869
	0.31 % O_2 used	Methane	16.043	1.48	357.41		
		Oxygen	32.0	0.755	66.09		
		Benzene	78.11	0.874	33.75	8.54	92.14/0.04118
	1.42% O_2 used	Methane	16.043	1.48	357.41		
		Oxygen	32.0	0.755	66.09		

*The costs of the largest quantities listed in the catalogue of Sigma-Aldrich was used for ACS reagent grade benzene (≥99 %, thiophene-free) and methanol ((≥99.8%), which are $AUS590/20 L and $1325/200 L, respectively. For methane, the cost of $1982.65 of Size G (= 8.21 m^3) of BOC Ultra Pure Grade Part No 149200 was used while for oxygen the cost of $AUS597.29 of Size G (= 6.21 m^3) of BOC Ultra High Purity Grade Part No 226200 was used.

Sample Calculations for Metric listed in Table 7 of Article

Atom Economy, AE (Reaction 15, Experiment 1):

$$\left(\frac{MW_{product}}{\Sigma MW_{reagents}}\right) \text{x } 100\% = \left(\frac{MW_{toluene}}{MW_{benzene} + MW_{methane} + 1/2MW_{oxygen}}\right) \text{x } 100\% = \left(\frac{92.14 \text{ x } 100}{78.11 + 16.043 + 1/2(32.0)}\right) = 83.6\%$$

Carbon Efficiency, CE (Reaction 15, Experiment 1):

$$\left(\frac{\text{no.of moles of product x no. of carbons in product x 100}}{\Sigma\text{moles of reagents x no. of carbons in reagent}}\right)\% = \left(\frac{\text{moles of toluene x 7 x 100}}{(\text{moles of benzene x 6}) + (\text{moles of methane x 1})}\right)\%$$

$$= \left(\frac{(0.01869/92.14) \text{ x } 700}{(2.181 \text{ x } 10^{-4} \text{ x } 6) + (2.181 \text{ x } 10^{-4} \text{ x } 1)}\right) = 93.0\%$$

Reaction Mass Efficiency, RME (Reaction 15, Experiment 1):

$$\left(\frac{\text{mass of product}}{\Sigma\text{mass of reagents}}\right) \text{x } 100\% = \left(\frac{\text{mass of toluene}}{(\text{mass of benzene} + \text{mass of methane} + \text{mass of oxygen})}\right) \text{x } 100\% = \left(\frac{0.01869 \text{ x } 100}{(0.01704 + 0.003499 + 0.003489)}\right) = 77.8\%$$

Effective Mass Yield, EMY (Reaction 15, Experiment 1):

$$\left(\frac{\text{mass of product}}{\Sigma\text{mass of non - benign reagents *}}\right) \text{x } 100\% = \left(\frac{\text{mass of toluene}}{(\text{mass of benzene} + \text{mass of oxygen})}\right) \text{x } 100\% = \left(\frac{0.01869 \text{ x } 100}{(0.01704 + 0.003489)}\right) = 91.1\%$$

*Non-benign reagents are those that are classified as hazardous substances in the MSDS according to the criteria of National Occupational Health and Safety Commission (NOHSC) of Australia, namely benzene and oxygen. In the case of the reaction 14, the methylation of benzene with methanol, methanol is also classified as hazardous substance.

Mass Intensity, MI (Reaction 15, Experiment 1):

$$\left(\frac{\text{Total mass used in a process or process step (kg)}}{\text{mass of product (kg)}}\right)=\left(\frac{\text{(mass of benzene + mass of methane + mass of oxygen + mass of catalyst) (kg)}}{\text{mass of toluene (kg)}}\right)$$

$$=\left(\frac{(0.01704+0.003499+0.003489+0.055)}{0.01869}\right)=4.23\text{ g/g}\equiv 4.23\text{ kg/kg}$$

Mass Productivity, MP (Reaction 15, Experiment 1):

$$\left(\frac{1}{\text{MI}}\text{ x }100\%\right)=\left(\frac{\text{mass of product x 100}}{\text{Total mass used in process or process step}}\right)=\left(\frac{\text{mass of toluene x 100}}{\text{(mass of benzene + mass of methane + mass of oxygen + mass of catalyst)}}\right)$$

$$=\left(\frac{0.01869}{(0.01704+0.003499+0.003489+0.055)}\right)=23.6\%$$

Raw Materials Cost, RMC (Reaction 15, Experiment 1):

$$\left(\frac{\text{mass of target product x }\Sigma(MW_{reagents}\text{ x Cost per g of reagent)}}{MW_{product}\text{ x Product yield}}\right)=\left(\frac{\Sigma(MW_{reagents}\text{ x Cost per kg of reagent)}}{MW_{product}\text{ x Product yield}}\right)=\$\text{/ kg product}$$

$$=\left(\frac{\left[(MW_{benzene}\text{ x Benzene cost/kg})+(MW_{methane}\text{ x Methane cost/kg})+(MW_{oxygen}\text{ x Oxygen cost/kg})\right]}{(MW_{toluene}\text{ x Toluene yield})}\right)$$

$$=\left(\frac{\left[(78.11\text{ x }33.75)+(16.043\text{ x }357.41)+(32.0\text{ x }66.09)\right]}{(92.14\text{ x }3.88/100)}\right)=\$2934.34\text{ / kg toluene}$$

Raw Materials Cost at 100% product yield, RMC_{100} (Reaction 15, Experiment 1):

RMC_{100} = RMC x Product yield = 2934.34 x (3.8781/100) = $113.80

ΔG Energy Intensity, ΔG-EI at 298 K (Reaction 15, Experiment 1):

$$\left(\frac{\Delta\text{G at 298 K}}{MW_{product}}\right) = \left(\frac{-185.8}{92.14}\right) = -\ 2.02\ \text{kJ/g} \equiv -\ 2.02\ \text{MJ/kg}$$

ΔH Energy Intensity, ΔH-EI at 298 K (Reaction 15, Experiment 1):

$$\left(\frac{\Delta\text{H at 298 K}}{MW_{product}}\right) = \left(\frac{-200.1}{92.14}\right) = -\ 2.17\ \text{kJ/g} \equiv -\ 2.17\ \text{MJ/kg}$$