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APPENDICES

Appendix A Gas and Oil Compositions from Using Pure Metal Oxide

Table A1 Gas and Oil Compositions from Using Metallic Tin and Tin Oxides with Different Oxidation States as a Catalyst

Catalyst	NonCat	Sn0	SnO	SnO2
Ethanol conversion (%)				
	97.4	98.1	97.8	98.8
Product distribution (wt%)				
Gas yield	97.0	97.7	97.7	97.6
Extracted oil yield	0.32	0.71	0.71	0.71
Non liquid oil yield	2.64	1.62	1.58	1.73
Gas composition (wt%)				
Methane	0.01	0.02	0.11	0.05
Ethylene	97.2	90.9	90.4	90.9
Ethane	0.57	0.66	1.00	0.86
Propylene	0.21	0.53	0.64	0.42
Propane	0.00	0.01	0.01	0.01
Butylene	1.87	6.77	7.49	7.33
Butane	0.18	1.09	0.36	0.48
Oil composition (wt%)				
Oxygenate compound	100	20.9	73.7	25.9
Non-aromatic	0	15.0	2.0	27.0
Benzene	0	64.1	24.2	47.1
Toluene	0	0	0	0
o-Xylene	0	0	0	0
m-Xylene	0	0	0	0
p-Xylene	0	0	0	0
Ethylbenzene	0	0	0	0
C9 Aromatics	0	0	0	0
C10+ Aromatics	0	0	0	0

Data were taken at the 1h of time-on-stream

Table A2 Gas and Oil Compositions from Using Metallic Antimony and Antimony Oxides with Different Oxidation States as a Catalyst

Catalyst	NonCat	Sb0	Sb2O3	Sb2O5
Ethanol conversion (%)				
	97.4	96.1	97.8	96.8
Product distribution (wt%)				
Gas yield	97.0	97.8	97.9	97.7
Extracted oil yield	0.32	0.67	0.67	0.67
Non liquid oil yield	2.64	1.53	1.43	1.59
Gas composition (wt%)				
Methane	0.01	-0.04	0.02	0.03
Ethylene	97.2	88.2	92.7	89.6
Ethane	0.57	0.86	0.68	0.69
Propylene	0.21	0.53	0.38	0.64
Propane	0.00	0.01	0.01	0.01
Butylene	1.87	9.34	5.41	7.81
Butane	0.18	1.06	0.76	1.26
Oil composition (wt%)				
Oxygenate compound	100	57.0	83.3	1.00
Non-aromatic	0	6.92	3.81	19.0
Benzene	0	36.1	12.8	81.0
Toluene	0	0	0	0
o-Xylene	0	0	0	0
m-Xylene	0	0	0	0
p-Xylene	0	0	0	0
Ethylbenzene	0	0	0	0
C9 Aromatics	0	0	0	0
C10+ Aromatics	0	0	0	0

Data were taken at the 1h of time-on-stream

Table A3 Gas and Oil Compositions from Using SAPO-34 as a Catalyst as a function of time on stream

Catalyst	SAPO34	SAPO34	SAPO34	SAPO34
Time-on-stream (min)	60	180	300	480
Ethanol conversion (%)				
	96.4	97.9	98.1	97.9
Product distribution (wt%)				
Gas yield	92.4	88.0	80.1	68.6
Extracted oil yield	1.2	1.4	1.8	2.0
Non liquid oil yield	6.37	10.7	18.1	29.4
Gas composition (wt%)				
Methane	0.18	0.19	0.19	0.08
Ethylene	92.0	93.2	93.3	95.6
Ethane	1.44	1.09	1.11	0.64
Propylene	2.61	1.72	1.38	0.44
Propane	0.58	0.59	0.38	0.06
Butylene	1.80	1.83	2.02	1.98
Butane	1.39	1.41	1.58	1.26
Oil composition (wt%)				
Oxygenate compound	44.5	19.2	56.0	52.1
Non-aromatic	0	2.94	0	0
Benzene	53.5	73.3	38.7	37.2
Toluene	0	0	0	0
o-Xylene	0	0	0	0
m-Xylene	0	0	0	0
p-Xylene	0	0	0	0
Ethylbenzene	0	0	0	0
C9 Aromatics	0	0	0	0
C10+ Aromatics	0	4.57	5.28	10.76

Table A4 Gas and Oil Compositions from Using 5 wt% tin oxide doped-SAPO-34 calcined at temperature 400 °C as a Catalyst as a function of time on stream

Catalyst	5SnSA34	5SnSA34	5SnSA34	5SnSA34
Time-on-stream (min)	60	180	300	480
Ethanol conversion (%)				
	97.1	97.8	97.8	98.3
Product distribution (wt%)				
Gas yield	95.8	92.6	78.0	61.7
Extracted oil yield	0.85	0.89	1.39	1.95
Non liquid oil yield	3.32	6.53	20.6	36.3
Gas composition (wt%)				
Methane	0.43	0.12	0.06	0.04
Ethylene	78.2	93.9	94.8	94.7
Ethane	1.66	0.65	0.45	0.39
Propylene	9.78	1.17	0.53	0.53
Propane	4.61	0.15	0.02	0.01
Butylene	2.89	2.32	2.67	3.03
Butane	2.40	1.74	1.52	1.34
Oil composition (wt%)				
Oxygenate compound	46.7	58.8	81.1	73.7
Non-aromatic	1.32	1.63	0.00	1.00
Benzene	51.9	39.6	18.6	11.1
Toluene	0	0	0	0
o-Xylene	0	0	0	0
m-Xylene	0	0	0.23	0
p-Xylene	0	0	0	0
Ethylbenzene	0	0	0	0.18
C9 Aromatics	0	0	0	0
C10+ Aromatics	0	0	0	14.0
Petroleum fraction (wt%)				
Gasoline	82.9	90.7	82.1	71.4
Kerosene	4.80	1.36	6.36	14.7
Gas oil	3.98	1.69	6.99	9.89
LVGO	0.54	0.43	0.57	0.50
HVGO	0	0	0	0

Table A5 Gas and Oil Compositions from Using 7 wt% tin oxide doped-SAPO-34 calcined at temperature 400 °C as a Catalyst as a function of time on stream

Catalyst	7SnSA34	7SnSA34	7SnSA34	7SnSA34
Time-on-stream (min)	60	180	300	480
Ethanol conversion (%)				
	98.0	96.4	97.0	97.6
Product distribution (wt%) -				
Gas yield	89.1	88.1	84.5	83.0
Extracted oil yield	1.93	0.70	1.31	0.77
Non liquid oil yield	8.93	11.2	14.2	16.2
Gas composition (wt%)				
Methane	0.96	0.27	0.47	0.22
Ethylene	51.7	88.7	84.7	90.9
Ethane	3.24	0.98	1.18	0.52
Propylene	20.3	2.93	3.71	1.95
Propane	13.45	0.91	0.86	0.12
Butylene	5.62	3.52	5.18	3.72
Butane	4.7	2.66	3.95	2.55
Oil composition (wt%)				
Oxygenate compound	13.4	43.9	9.04	19.3
Non-aromatic	0	0	0	0
Benzene	72.0	56.1	60.6	63.6
Toluene	0	0	0	0
o-Xylene	0	0	0	0
m-Xylene	0	0	0	0
p-Xylene	0	0	0	0
Ethylbenzene	0	0	0	0
C9 Aromatics	0	0	0	0
C10+ Aromatics	14.5	0	30.3	17.1
Petroleum fraction (wt%)				
Gasoline	92.2	76.1	75.6	52.2
Kerosene	2.57	8.42	12.3	22.4
Gas oil	1.81	6.89	7.7	21.4
LVGO	0.42	0.55	0.57	0.53
HVGO	0	0	0	0

Table A6 Gas and Oil Compositions from Using 5 wt% antimony oxide doped-SAPO-34 calcined at temperature 400 °C as a Catalyst as a function of time on stream

Catalyst	5SbSA34	5SbSA34	5SbSA34	5SbSA34
Time-on-stream (min)	60	180	300	480
Ethanol conversion (%)				
	93.1	96.7	96.8	97.8
Product distribution (wt%)				
Gas yield	92.72	83.73	67.78	61.91
Extracted oil yield	0.18	1.97	1.44	2.10
Non liquid oil yield	7.11	14.3	30.8	36.0
Gas composition (wt%)				
Methane	0.70	0.19	0.12	0.13
Ethylene	58.2	91.8	92.5	93.1
Ethane	3.14	1.10	0.78	0.62
Propylene	17.5	1.05	0.68	0.86
Propane	13.8	0.20	0.06	0.02
Butylene	3.39	3.27	3.55	4.76
Butane	3.29	2.42	2.32	0.46
Oil composition (wt%)				
Oxygenate compound	7.74	29.8	63.2	66.2
Non-aromatic	1.91	1.38	0.17	0.85
Benzene	42.2	9.36	3.73	12.4
Toluene	0	0	0.16	0
o-Xylene	0	0	1.52	0
m-Xylene	0	0	0	0
p-Xylene	0	0.26	0	0
Ethylbenzene	0	0	0	0.18
C9 Aromatics	0	0	0.08	0
C10+ Aromatics	48.1	59.2	31.1	20.4
Petroleum fraction (wt%)				
Gasoline	77.2	77.6	71.4	56.5
Kerosene	2.49	6.73	9.43	11.6
Gas oil	6.95	7.51	15.4	27.7
LVGO	0.52	0.52	0.49	0.82
HVGO	0	0	0	0

Table A7 Gas and Oil Compositions from Using 7 wt% antimony oxide doped-SAPO-34 calcined at temperature 400 °C as a Catalyst as a function of time on stream

Catalyst	7SbSA34	7SbSA34	7SbSA34	7SbSA34
Time-on-stream (min)	60	180	300	480
Ethanol conversion (%)				
	95.7	96.8	98.3	98.0
Product distribution (wt%)				
Gas yield	91.8	81.0	71.1	61.8
Extracted oil yield	1.42	1.20	2.01	0.74
Non liquid oil yield	6.79	17.9	26.9	37.4
Gas composition (wt%)				
Methane	0.85	0.10	0.06	0.04
Ethylene	66.0	94.2	95.8	93.9
Ethane	2.95	0.65	0.49	0.49
Propylene	14.4	0.48	0.35	0.41
Propane	9.94	0.04	0.02	0.01
Butylene	3.26	2.84	2.14	3.71
Butane	2.60	1.73	1.15	1.43
Oil composition (wt%)				
Oxygenate compound	16.8	28.1	0.44	71.5
Non-aromatic	7.30	1.76	0.40	2.77
Benzene	75.9	16.3	0.99	10.2
Toluene	0	0	0	0
o-Xylene	0	0	0.034	0
m-Xylene	0	0	0	0
p-Xylene	0	0	0	0
Ethylbenzene	0	0	0	0
C9 Aromatics	0	0	0	0
C10+ Aromatics	0	53.9	98.1	15.5
Petroleum fraction (wt%)				
Gasoline	95.8	79.8	43.2	82.4
Kerosene	0.97	15.1	39.4	8.29
Gas oil	1.29	0	13.8	5.87
LVGO	0.33	0	0.52	0.46
HVGO	0	0	0	0

Table A8 Gas and Oil Compositions from Using 5 wt% tin oxide doped-SAPO-34 calcined at temperature 700 °C as a Catalyst as a function of time on stream

Catalyst	5SnSA34	5SnSA34	5SnSA34	5SnSA34
Time-on-stream (min)	60	180	300	480
Ethanol conversion (%)				
	96.4	97.9	98.1	97.9
Product distribution (wt%)				
Gas yield	93.6	89.3	81.9	70.6
Extracted oil yield	1.21	1.39	1.79	2.00
Non liquid oil yield	5.16	9.28	16.3	27.4
Gas composition (wt%)				
Methane	0.46	0.21	0.05	0.07
Ethylene	81.9	93.2	94.3	94.9
Ethane	2.02	1.09	0.63	0.78
Propylene	3.05	1.27	0.36	0.30
Propane	2.72	0.55	0.02	0.02
Butylene	5.72	2.06	3.55	3.24
Butane	4.12	1.59	1.13	0.72
Oil composition (wt%)				
Oxygenate compound	56.3	42.4	83.6	86.2
Non-aromatic	1.52	2.12	0	0
Benzene	42.2	55.5	11.7	3.4
Toluene	0	0	0	0
o-Xylene	0	0	0	0
m-Xylene	0	0	0	0
p-Xylene	0	0	0	0
Ethylbenzene	0	0	0	0
C9 Aromatics	0	0	0	0
C10+ Aromatics	0	0	4.72	10.4
Petroleum fraction (wt%)				
Gasoline	90.3	91.7	86.2	92.0
Kerosene	1	2.13	5.84	2.84
Gas oil	1.33	2.28	4.37	2.07
LVGO	0.33	0.46	0.48	0.5
HVGO	0	0	0	0

Table A9 Gas and Oil Compositions from Using 7 wt% tin oxide doped-SAPO-34 calcined at temperature 700 °C as a Catalyst as a function of time on stream

Catalyst	7SnSA34	7SnSA34	7SnSA34	7SnSA34
Time-on-stream (min)	60	180	300	480
Ethanol conversion (%)				
	97.3	97.9	97.9	97.9
Product distribution (wt%)				
Gas yield	90.3	84.1	78.6	72.4
Extracted oil yield	0.79	0.77	1.24	1.46
Non liquid oil yield	8.88	15.1	20.1	26.1
Gas composition (wt%)				
Methane	0.22	0.12	0.07	0.06
Ethylene	89.6	94.8	95.1	94.6
Ethane	1.34	0.79	0.59	0.57
Propylene	2.44	0.56	0.39	0.37
Propane	1.48	0.16	0.03	0.01
Butylene	2.75	2.02	2.35	3.17
Butane	2.14	1.55	1.45	1.25
Oil composition (wt%)				
Oxygenate compound	68.1	47.6	43.4	43.2
Non-aromatic	1.38	5.82	0.17	0.21
Benzene	29.0	10.7	9.62	3.42
Toluene	0	0	0	0
o-Xylene	0	0	0	0
m-Xylene	0	12.87	0	0.12
p-Xylene	0	22.3	0	0
Ethylbenzene	0	0.69	0	0
C9 Aromatics	0	0	0	0.239
C10+ Aromatics	1.51	0	46.8	52.8
Retroleum fraction (wt%)				
Gasoline	82.1	69.2	87.3	75.1
Kerosene	9.17	23.5	5.07	16.9
Gas oil	5.23	4.12	4.47	4.59
LVGO	0.61	1.24	0.84	0.46
HVGO	0	0	0	0

Table A10 Gas and Oil Compositions from Using 5 wt% antimony oxide doped-SAPO-34 calcined at temperature 700 °C as a Catalyst as a function of time on stream

Catalyst	5SbSA34	5SbSA34	5SbSA34	5SbSA34
Time-on-stream (min)	60	180	300	480
Ethanol conversion (%)				
	99.1	97.7	98.6	98.4
Product distribution (wt%)				
Gas yield	98.4	88.8	78.9	72.0
Extracted oil yield	0.44	0.53	0.87	1.22
Non liquid oil yield	1.20	10.7	20.2	26.8
Gas composition (wt%)				
Methane	0.36	0.15	0.05	0.04
Ethylene	87.1	94.1	95.9	95.9
Ethane	1.64	0.85	0.55	0.53
Propylene	4.17	0.71	0.34	0.32
Propane	2.45	0.12	0.02	0.01
Butylene	2.35	2.28	1.85	1.96
Butane	1.93	1.78	1.26	1.27
Oil composition (wt%)				
Oxygenate compound	26.5	85.0	72.9	89.6
Non-aromatic	0	0	0.69	0
Benzene	73.5	15.0	26.5	10.4
Toluene	0	0	0	0
o-Xylene	0	0	0	0
m-Xylene	0	0	0	0
p-Xylene	0	0	0	0
Ethylbenzene	0	0	0	0
C9 Aromatics	0	0	0	0
C10+ Aromatics	0	0	0	0
Petroleum fraction (wt%)				
Gasoline	90.8	92.9	78.8	79.5
Kerosene	0.90	2.59	6.97	8.47
Gas oil	1.21	1.50	9.46	8.96
LVGO	0.30	0.38	1.26	1.14
HVGO	0	0	0	0

Table A11 Gas and Oil Compositions from Using 7 wt% antimony oxide doped-SAPO-34 calcined at temperature 700 °C as a Catalyst as a function of time on stream

Catalyst	7SbSA34	7SbSA34	7SbSA34	7SbSA34
Time-on-stream (min)	60	180	300	480
Ethanol conversion (%)				
	96.4	97.9	98.1	97.9
Product distribution (wt%)				
Gas yield	95.3	89.0	77.5	76.7
Extracted oil yield	0.47	0.42	0.55	1.55
Non liquid oil yield	4.28	10.6	22.0	21.8
Gas composition (wt%)				
Methane	0.21	0.03	0.03	0.07
Ethylene	93.6	95.4	96.1	94.9
Ethane	1.01	0.56	0.45	0.78
Propylene	1.60	0.34	0.31	0.30
Propane	0.85	0.01	0.01	0.02
Butylene	1.55	2.14	1.76	3.24
Butane	1.21	1.48	1.33	0.72
Oil composition (wt%)				
Oxygenate compound	22.6	49.8	34.0	77.5
Non-aromatic	77.4	35.3	45.7	17.6
Benzene	0	14.9	20.4	4.86
Toluene	0	0	0	0
o-Xylene	0	0	0	0
m-Xylene	0	0	0	0
p-Xylene	0	0	0	0
Ethylbenzene	0	0	0	0
C9 Aromatics	0	0	0	0
C10+ Aromatics	0	0	0	0
Petroleum fraction (wt%)				
Gasoline	90.9	92.2	90.5	91.2
Kerosene	1.01	2.69	4.28	4.14
Gas oil	1.15	1.75	1.93	1.63
LVGO	0.32	0.12	0.44	0.41
HVGO	0	0	0	0

Appendix B Species and Surface Composition on Unsupported Catalysts

Table B1 Species of Tin on Fresh and Spent Sn⁰, SnO and SnO₂

Name		Composition (%)			
		-OH	Sn ⁺⁴	Sn ⁺²	Sn ⁰
Metallic tin	Fresh	0	0	0	100
	Spent	0	87	0	13
SnO	Fresh	4	0	93	3
	Spent	4	0	93	3
SnO ₂	Fresh	3	97	0	0
	Spent	9	89	0	2

Table B2 Species of Tin on Fresh and Spent Sb⁰, Sb₂O₃ and Sb₂O₅

Name		Composition (%)			
		Sb ₂ O ₅ ·H ₂ O	Sb ⁺⁵	Sb ⁺³	Sb ⁰
Metallic Sb	Fresh	0	0	49	51
	Spent	0	0	86	14
Sb ₂ O ₃	Fresh	0	38	62	0
	Spent	0	46	54	0
Sb ₂ O ₅	Fresh	22	78	0	0
	Spent	23	77	0	0

Appendix C Species and Surface Composition on Supported Catalysts

Table C1 Species of Tin and Composition on 5 wt% Tin Oxide-Doped SAPO-34
Calcined at temperature 400 °C

5SnSAPO34-400	Composition (%)		
	-OH	Sn ⁺⁴	Sn ⁰
Fresh	14	86	0
60 min	62	38	0
180 min	19	58	23
300 min	16	62	22
480 min	0	47	53

Table C2 Species of Tin and Composition on 7 wt% Tin Oxide-Doped SAPO-34
Calcined at temperature 400 °C

7SnSAPO34-400	Composition (%)		
	-OH	Sn ⁺⁴	Sn ⁰
Fresh	22	78	0
60 min	0	39	61
180 min	0	63	37
300 min	0	36	67
480 min	0	81	19

Table C3 Species of Antimony and Composition on 5 wt% Antimony Oxide-Doped
SAPO-34 Calcined at temperature 400 °C

5SbSAPO34-400	Composition(%)	
	Sb ⁺⁵	Sb ⁺³
Fresh	54	46
60 min	40	60
180 min	56	44
300 min	63	37
480 min	52	48

Table C5 Species of Antimony and Composition on 7 wt% Antimony Oxide-Doped SAPO-34 Calcined at temperature 400 °C

7SbSAPO34-400	Compostion(%)	
	Sb ⁺⁵	Sb ⁺³
Fresh	41	59
60 min	40	60
180 min	30	70
300 min	34	66
480 min	29	71

Table C6 Species of Tin and Composition on 5 wt% Tin Oxide-Doped SAPO-34 Calcined at temperature 700 °C

5SnSAPO34-700	Compostion(%)			
	-OH	Sn ⁺⁴	Sn ⁺²	Sn ⁰
Fresh	20	0	80	0
60 min	15	11	0	74
180 min	0	17	0	83
300 min	0	32	0	68
480 min	0	15	0	85

Table C7 Species of Tin and Composition on 7 wt% Tin Oxide-Doped SAPO-34 Calcined at temperature 700 °C

5SnSAPO34-700	Compostion(%)			
	-OH	Sn ⁺⁴	Sn ⁺²	Sn ⁰
Fresh	61	0	39	0
60 min	0	22	0	78
180 min	0	25	0	75
300 min	0	33	0	67
480 min	0	32	0	67

Table C8 Species of Antimony and Composition on 5 wt% Antimony Oxide-Doped SAPO-34 Calcined at temperature 700 °C

5SbSAPO34-700	Compostion(%)	
	Sb ⁺⁵	Sb ⁺³
Fresh	65	35
60 min	34	66
180 min	27	73
300 min	50	50
480 min	59	41

Table C9 Species of Antimony and Composition on 7 wt% Antimony Oxide-Doped SAPO-34 Calcined at temperature 700 °C

7SbSAPO34-700	Compostion(%)	
	Sb ⁺⁵	Sb ⁺³
Fresh	30	70
60 min	39	61
180 min	46	54
300 min	43	57
480 min	51	49

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