Supplemental Information

Continuous Upgrading of Fast Pyrolysis Oil by Simultaneous Esterification and Hydrogenation

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Supporting Information.

1. Catalyst Characterization Results
2. GC/MS Chromatograms
3. Catalyst Coke Analysis

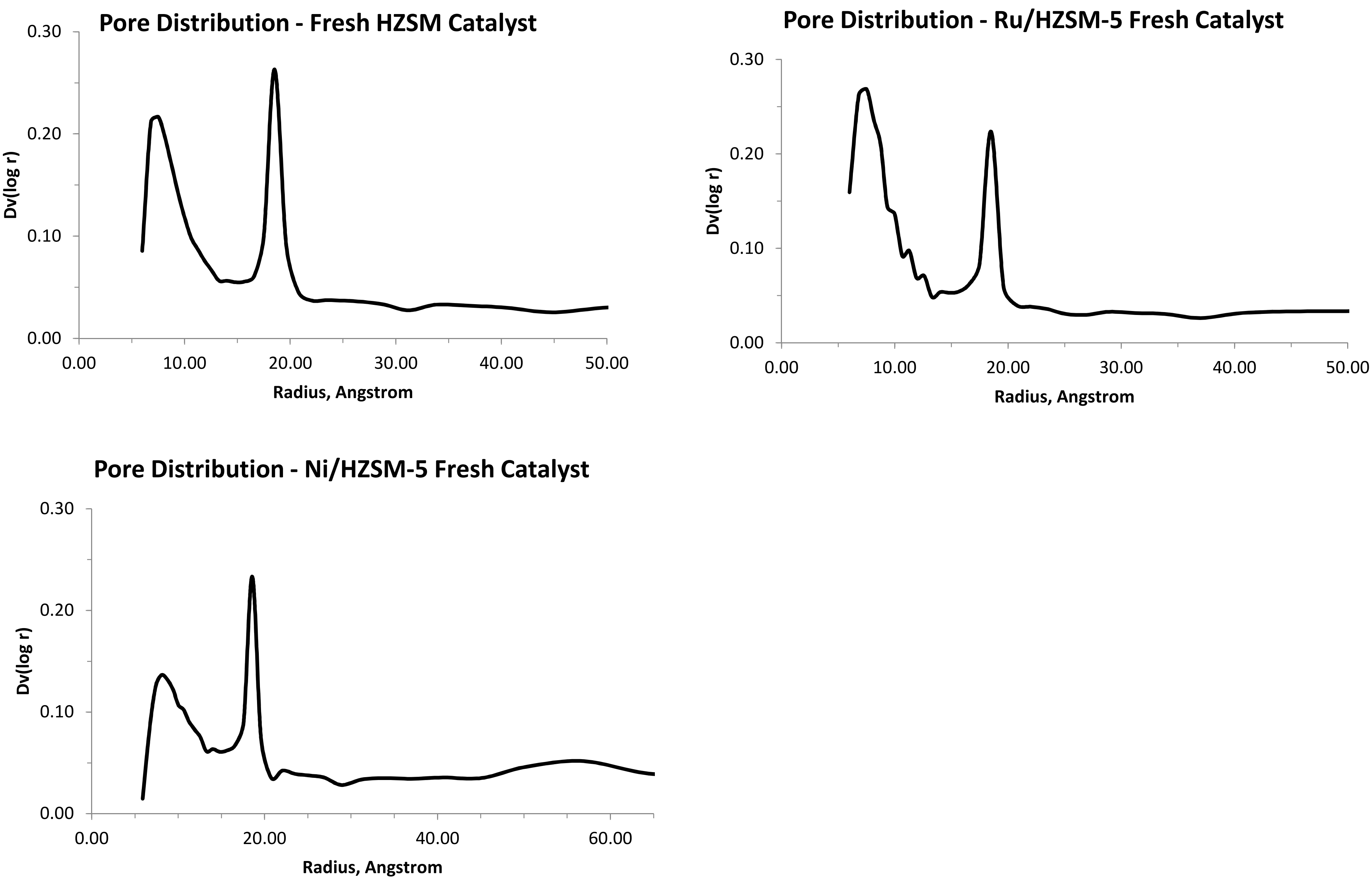
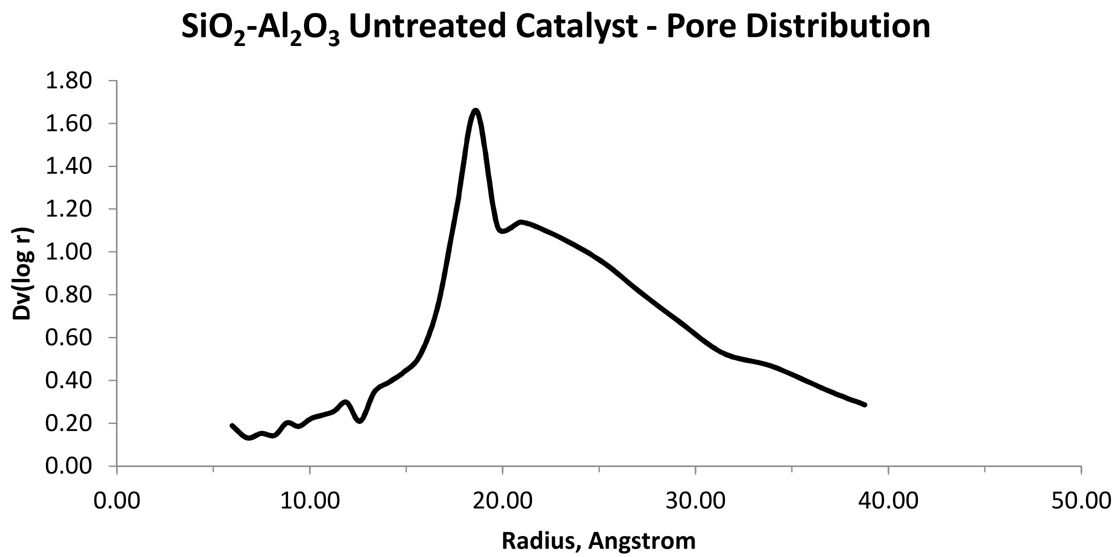


Figure 1S: Pore size distribution (BJH method) for freshly prepared catalysts.



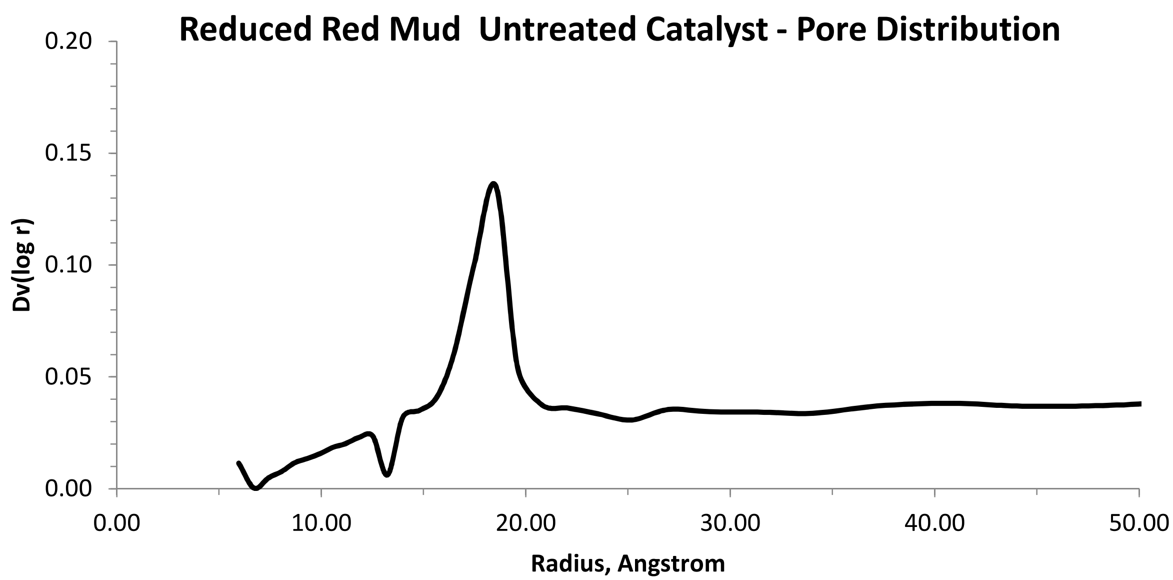


Figure 1S - Continued: Pore size distribution (BJH method) for freshly prepared catalysts.

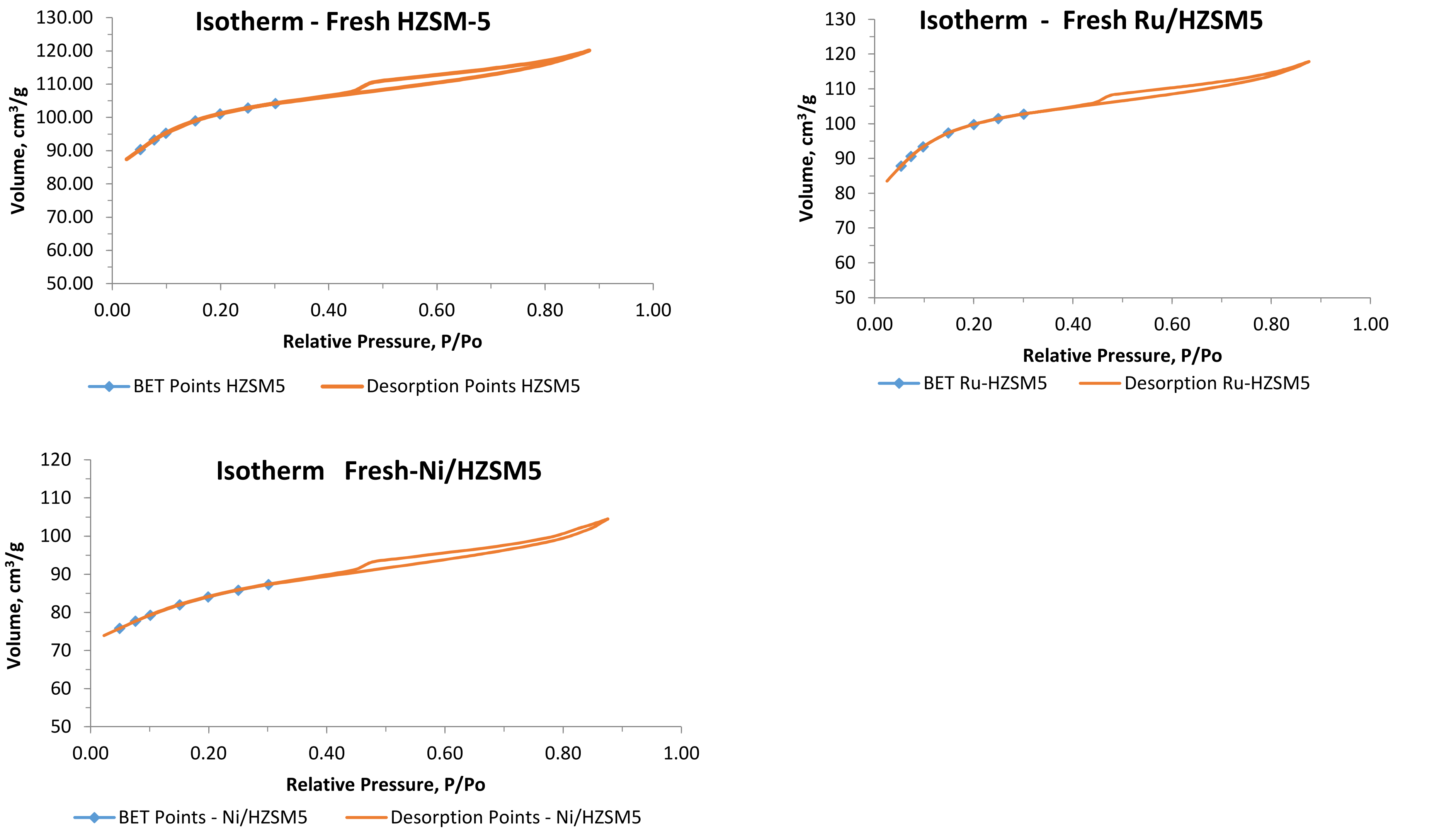
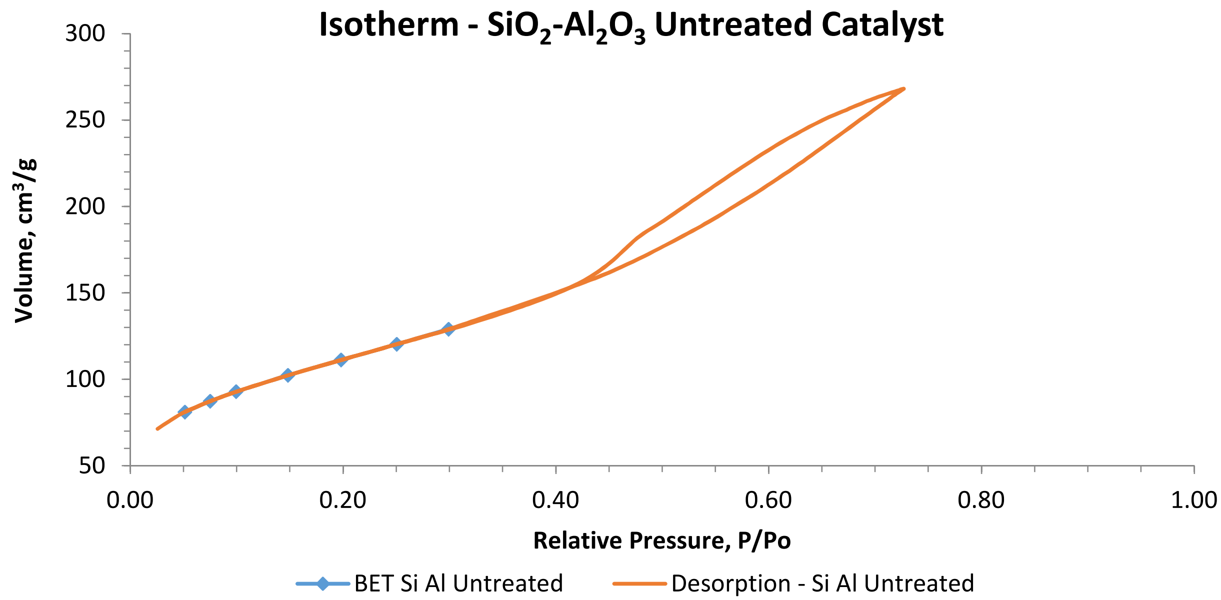


Figure 2S: Nitrogen adsorption isotherms for freshly prepared catalysts.



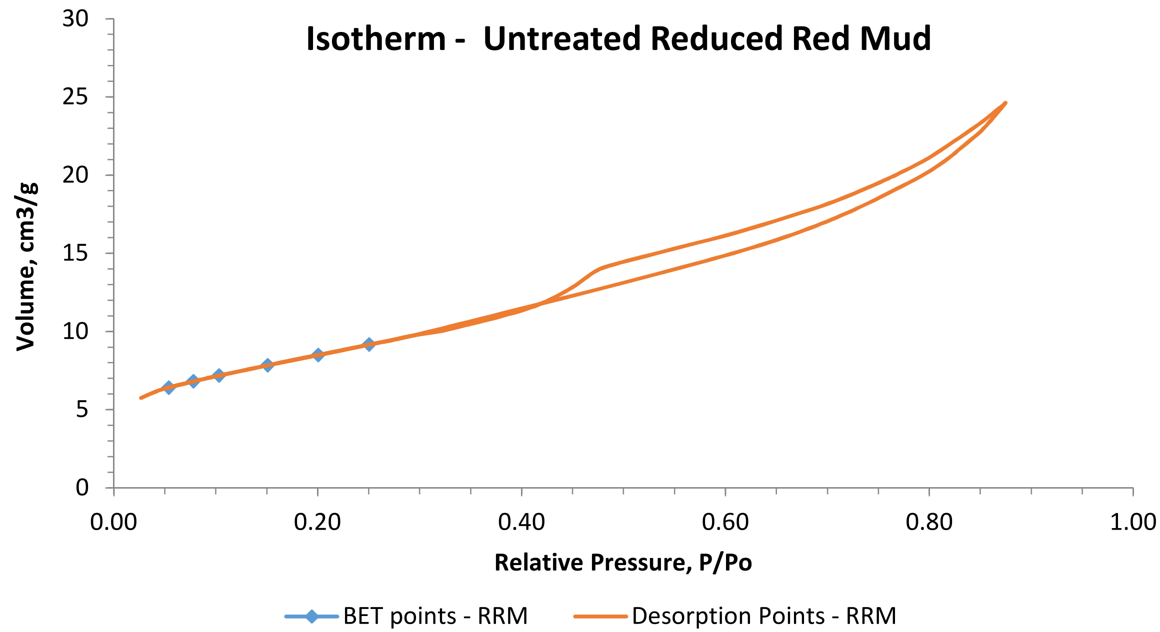


Figure 2S - Continued: Nitrogen adsorption isotherms for freshly prepared catalysts.

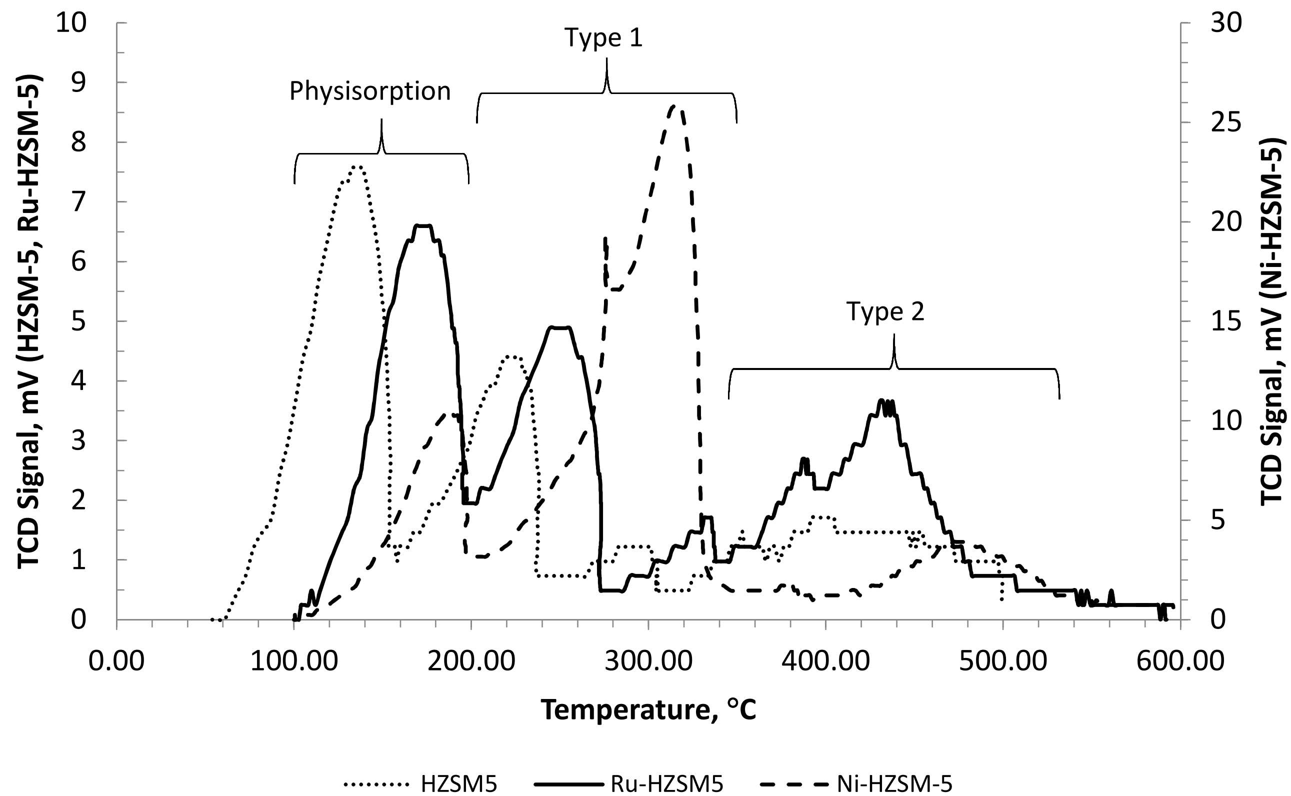


Figure 3S: Ammonia TPD analysis of freshly prepared HZSM-5, Ru-HSZM-5, and Ni-HZSM-5 (RRM and SiO_2-Al_2O_3 not shown).

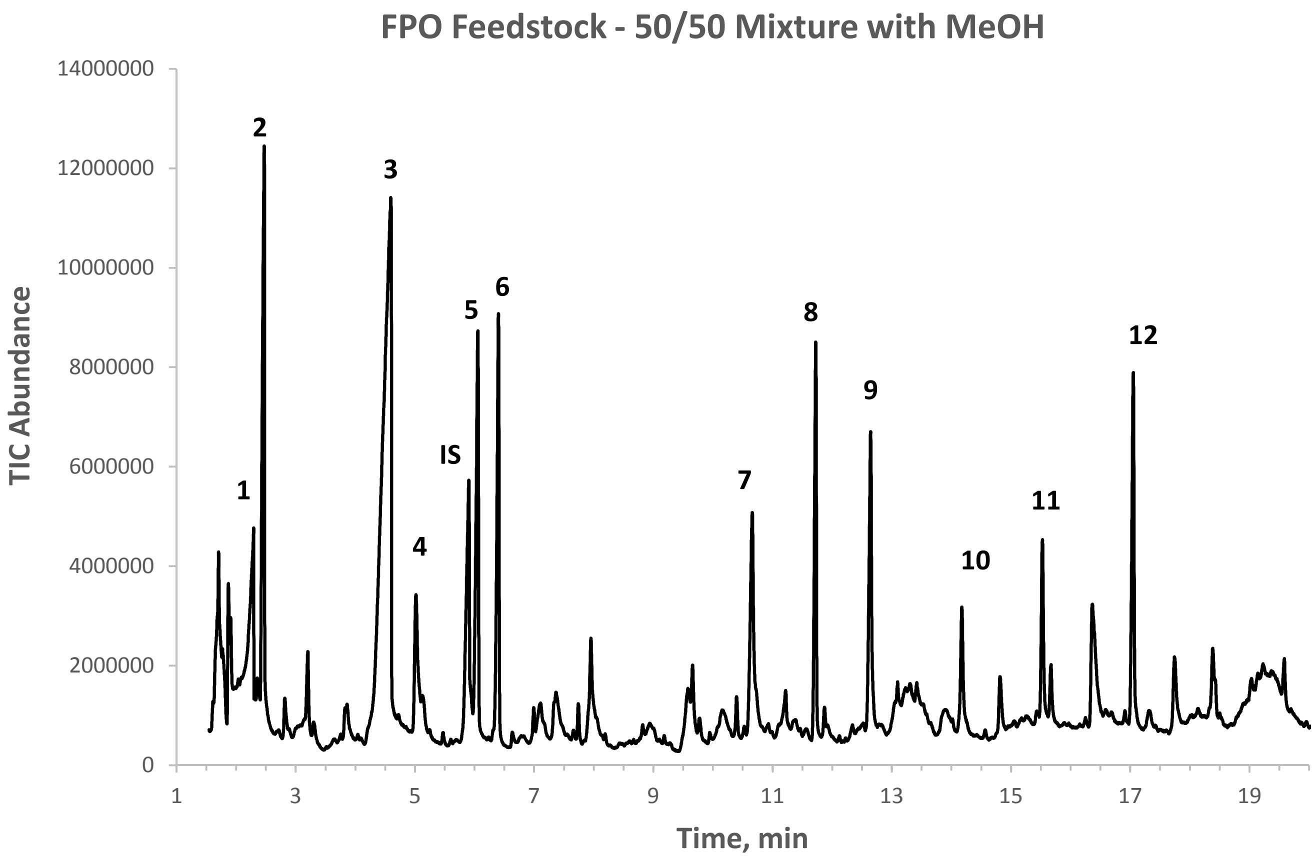


Figure 4S: GC/MS analysis of FPO feedstock (50/50 mixture of oil and methanol) with a solvent delay. Note, the analysis continues to 40 min, but is not shown here, due to the presence of small unidentifiable peaks (i.e., low match factors). (1) acetic acid, (2) acetol, (3) glycolaldehyde dimethyl acetal, (4) furfural, (IS) hexanol, (5) furan, tetrahydro-2,5-dimethoxy-, (6) furan, tetrahydro-2,5-dimethoxy-, (7) phenol, 2-methoxy-, (8) hexanal dimethyl acetal, (9) phenol, 2-methoxy-4-methyl-, (10) phenol, 4-ethyl-2-methoxy-, (11) eugenol, (12) phenol, 2-methoxy-4-(1-propenyl)-, (E)-

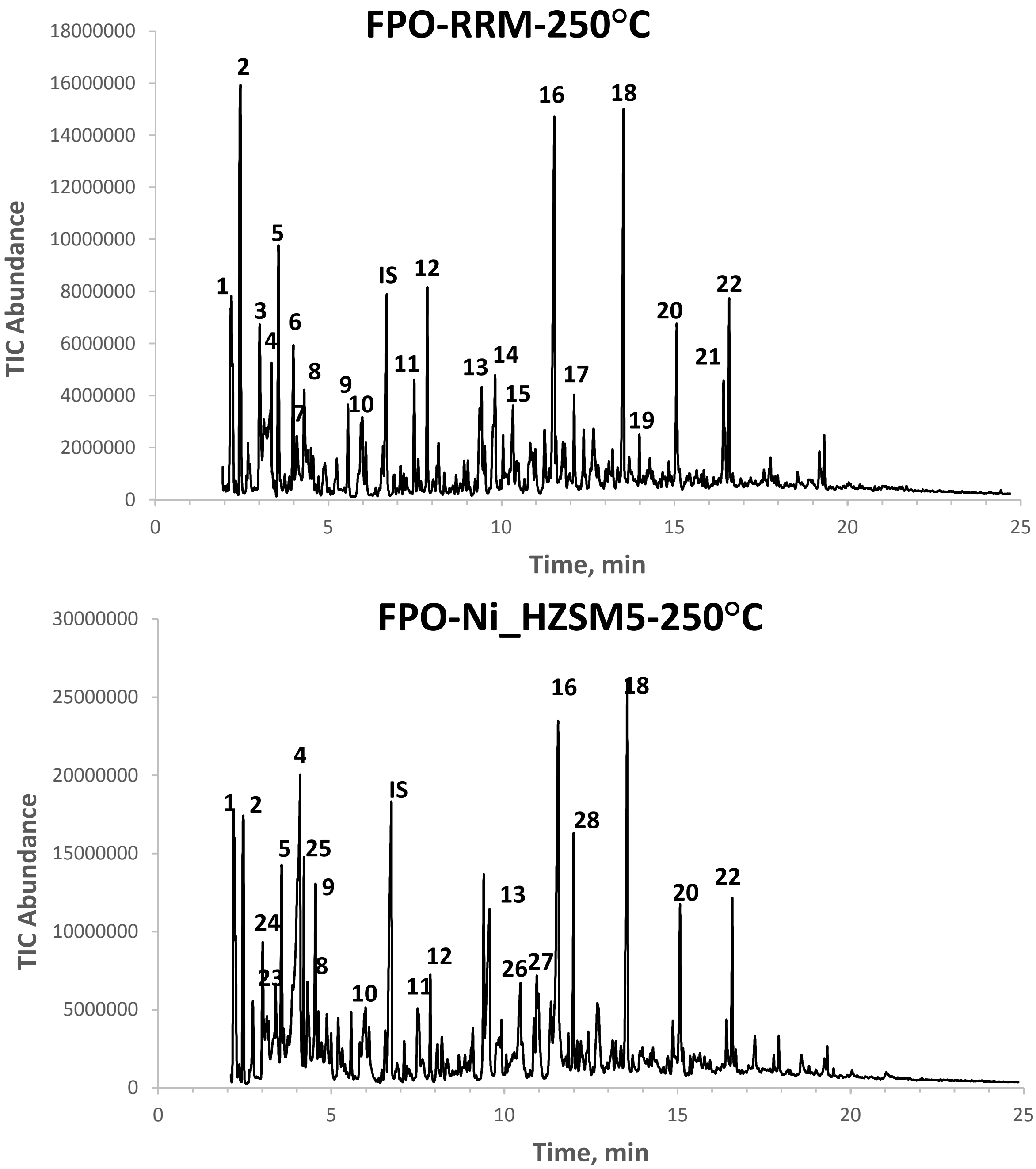
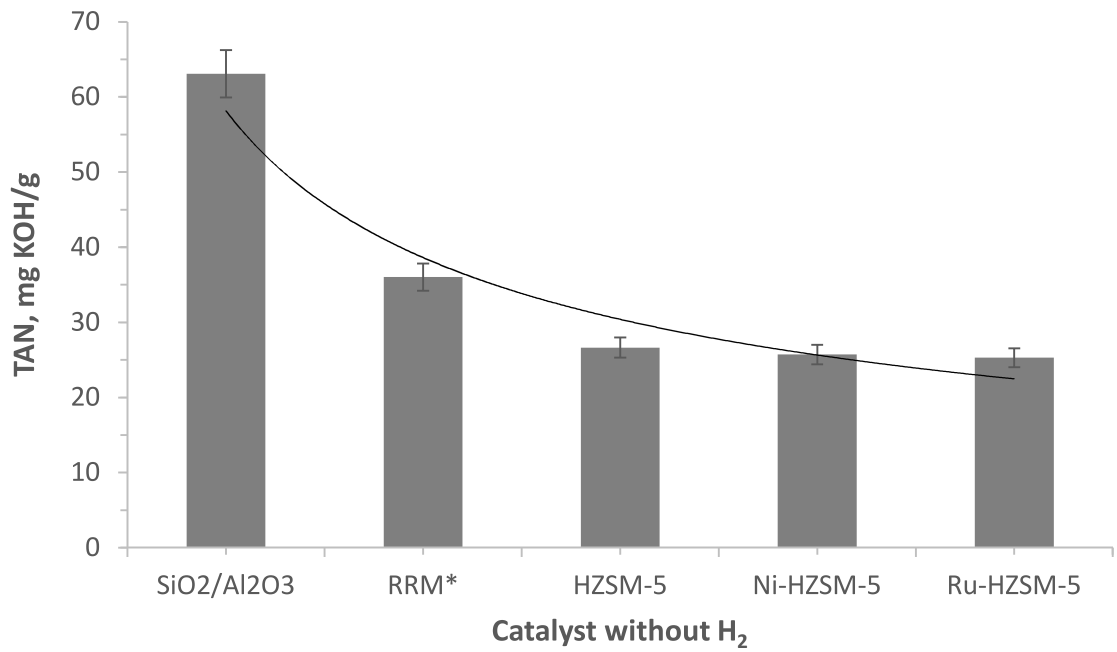


Figure 5S: GC/MS analysis of product from catalytic esterification using RRM and Ni-HZSM-5 of a FPO feedstock (50/50 mixture of oil and methanol) with a solvent delay. Note, the analysis continues to 40 min, but is not shown here, due to the presence of small unidentifiable peaks (i.e., low match factors). (1) ethane, 1,1-dimethoxy-, (2) methyl propionate, (3) propanoic acid, 2-methyl-, methyl ester, (4) acetic acid, (5) butanoic acid, methyl ester, (6) Acetic acid, hydroxy-, methyl ester, (7) 2-methoxytetrahydrofuran, (8) 2-butenoic acid, methyl ester, (E)-, (9) pentanoic acid, methyl ester, (IS) hexanol, (10) Cyclopentanone, 2-methyl-, (11) 2-Cyclopenten-1-one, 2-methyl-, (12) hexanoic acid, methyl ester, (13) pentanoic acid, 4-oxo-, methyl ester, (14) propanoic acid, 2-methyl-, anhydride, (15) heptanoic acid, methyl ester, (16) phenol, 2-methoxy-, (17) octanoic acid, methyl ester, (18) phenol, 2-methoxy-4-methyl-, (19) nonanoic acid, methyl ester, (20) phenol, 4-ethyl-2-methoxy-, (21) phenol, 2-methoxy-4-(1-propenyl)-, (E)-, (22) Phenol, 2-methoxy-4-propyl-, (23) 2-butanone, 3-methyl-, (24) propane, 1,1-dimethoxy-, (25) 2-propanone, 1-hydroxy-, (26) 2-Cyclopenten-1-one, 2-hydroxy-3-methyl, (27) Ethanone, 1-(1-cyclohexen-1-yl)-, (28) Benzene, 1,2,4,5-tetramethyl-.



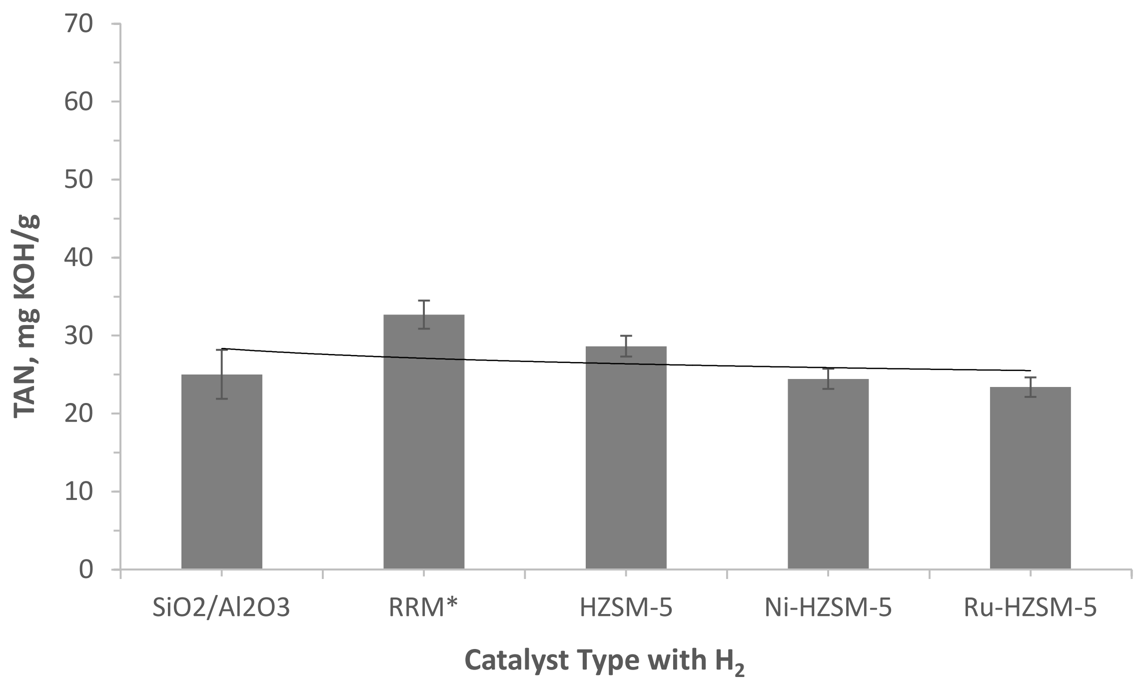


Figure 6S: Measured TAN values for collected liquid products from catalytic esterification of FPO/methanol mixture at 250°C and 600 psig (W/F = 0.4 h) with (bottom) and without H_2 (top). The TAN value for the feedstock was 98.7± 14.1 mg KOH/g.

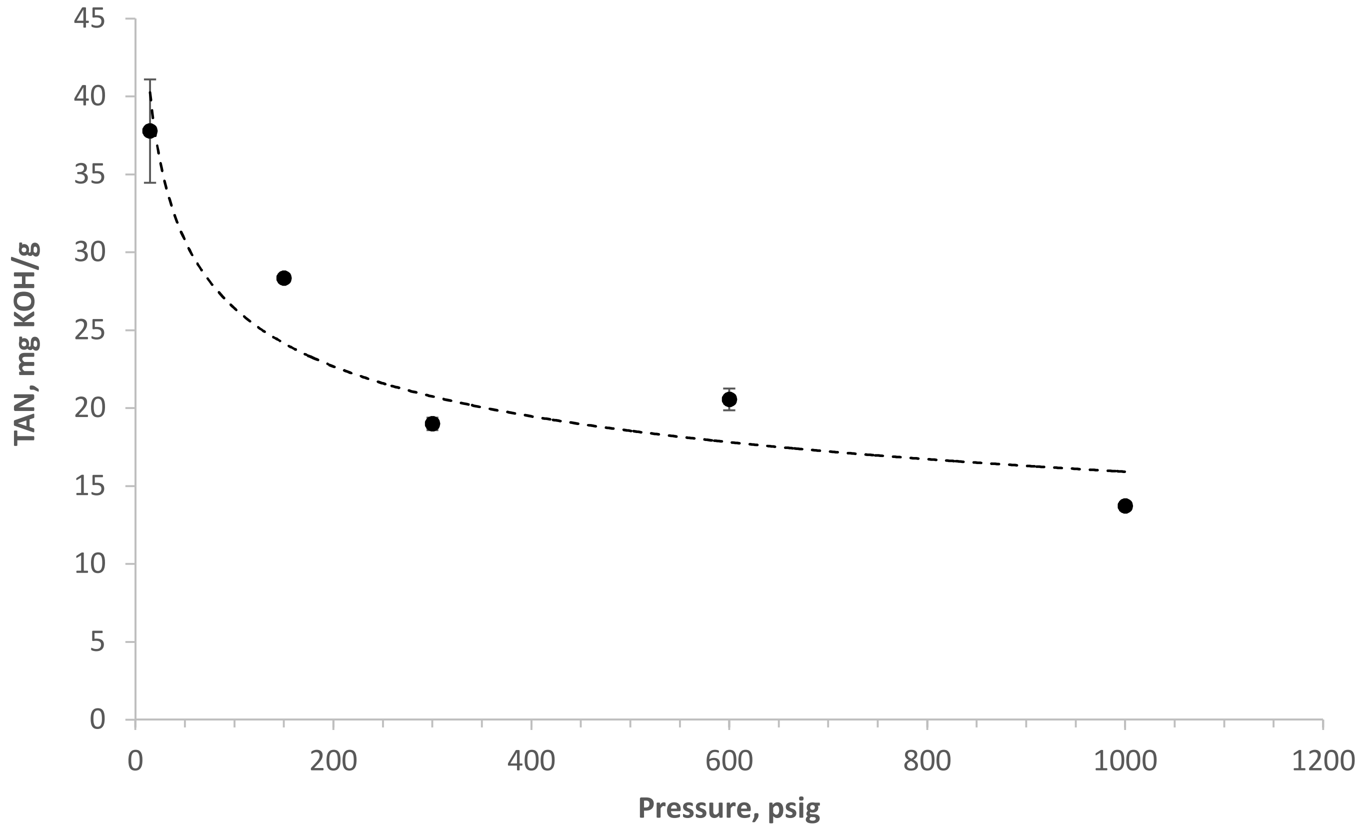


Figure 7S: Measured TAN values for collected liquid products from catalytic esterification of FPO/methanol mixture at 250°C over a range of pressures (W/F = 0.92 h). The TAN value for the feedstock was 98.7± 14.1 mg KOH/g.

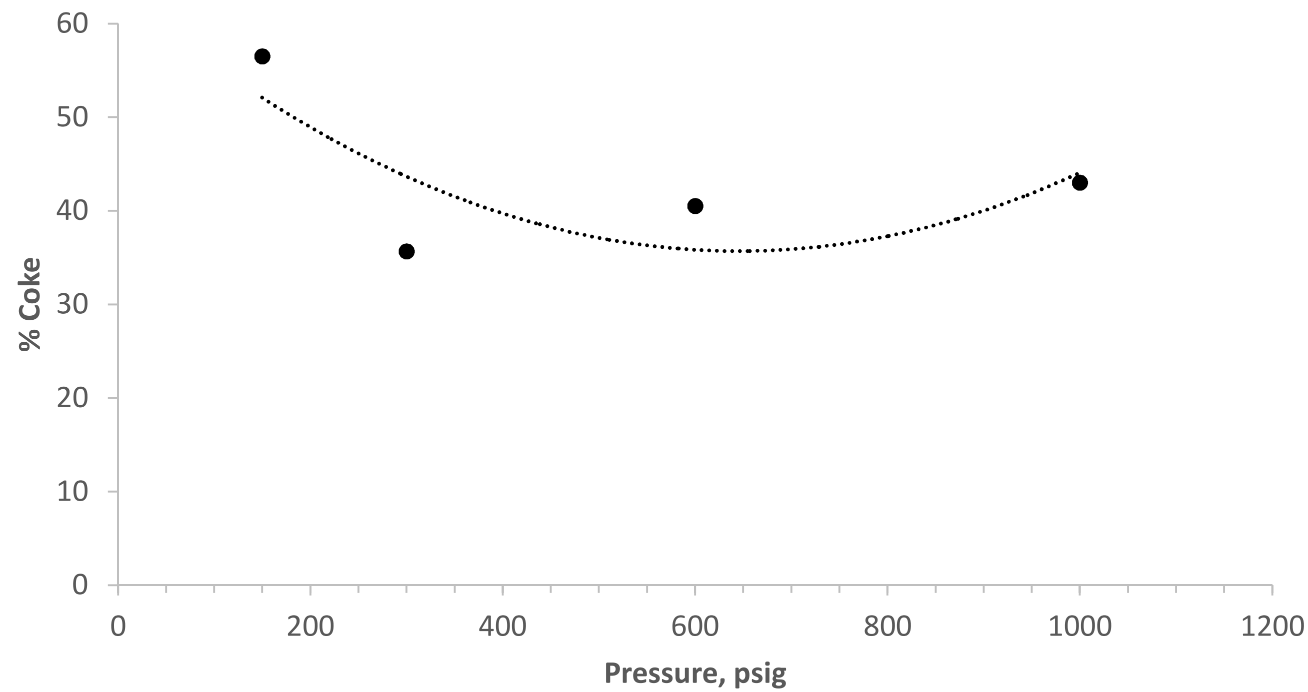


Figure 8S: Effect of pressure on coke formation for catalytic esterification of an FPO/methanol mixture using RRM (250°C).

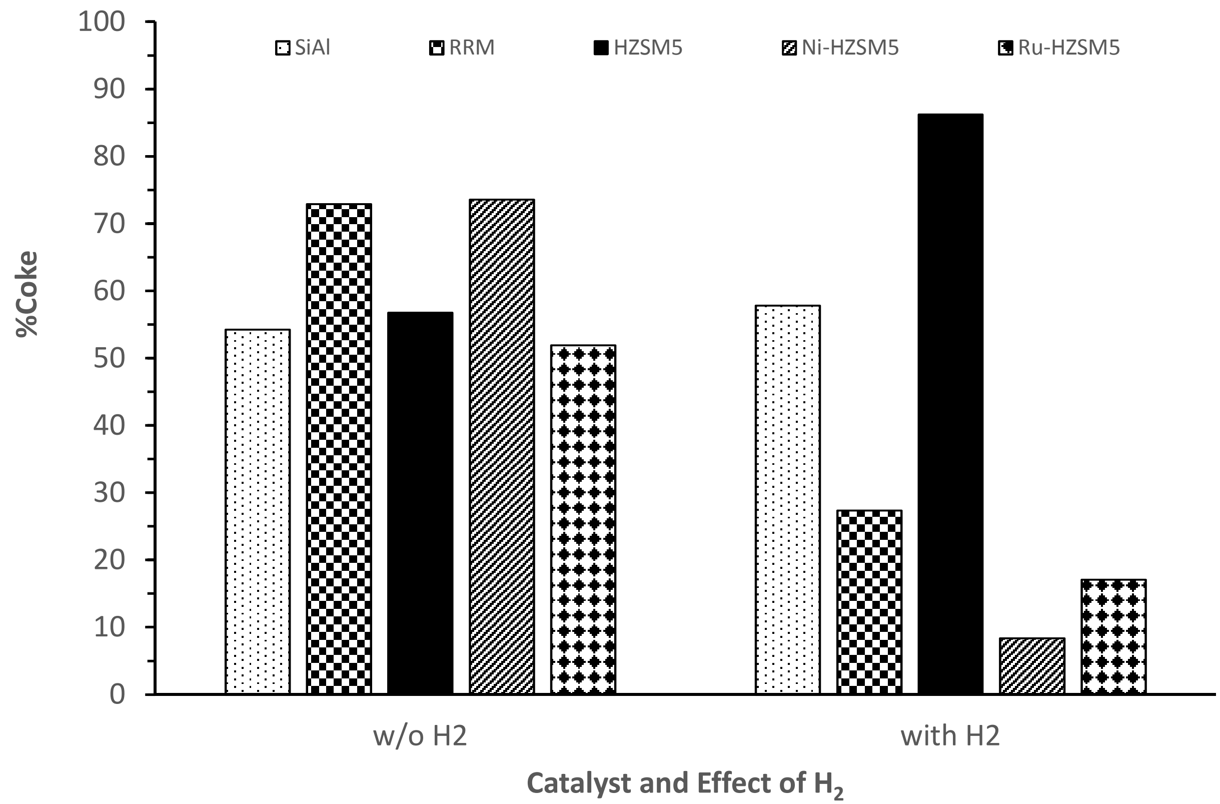


Figure 9S: Effect of H_2 on coke formation measured via TGA during catalytic esterification/hydrogenation of FPO mixed with methanol (1:1[v/v]) using SiAl, RRM, HZSM-5, Ni-HZSM5, and Ru-HZSM-5.

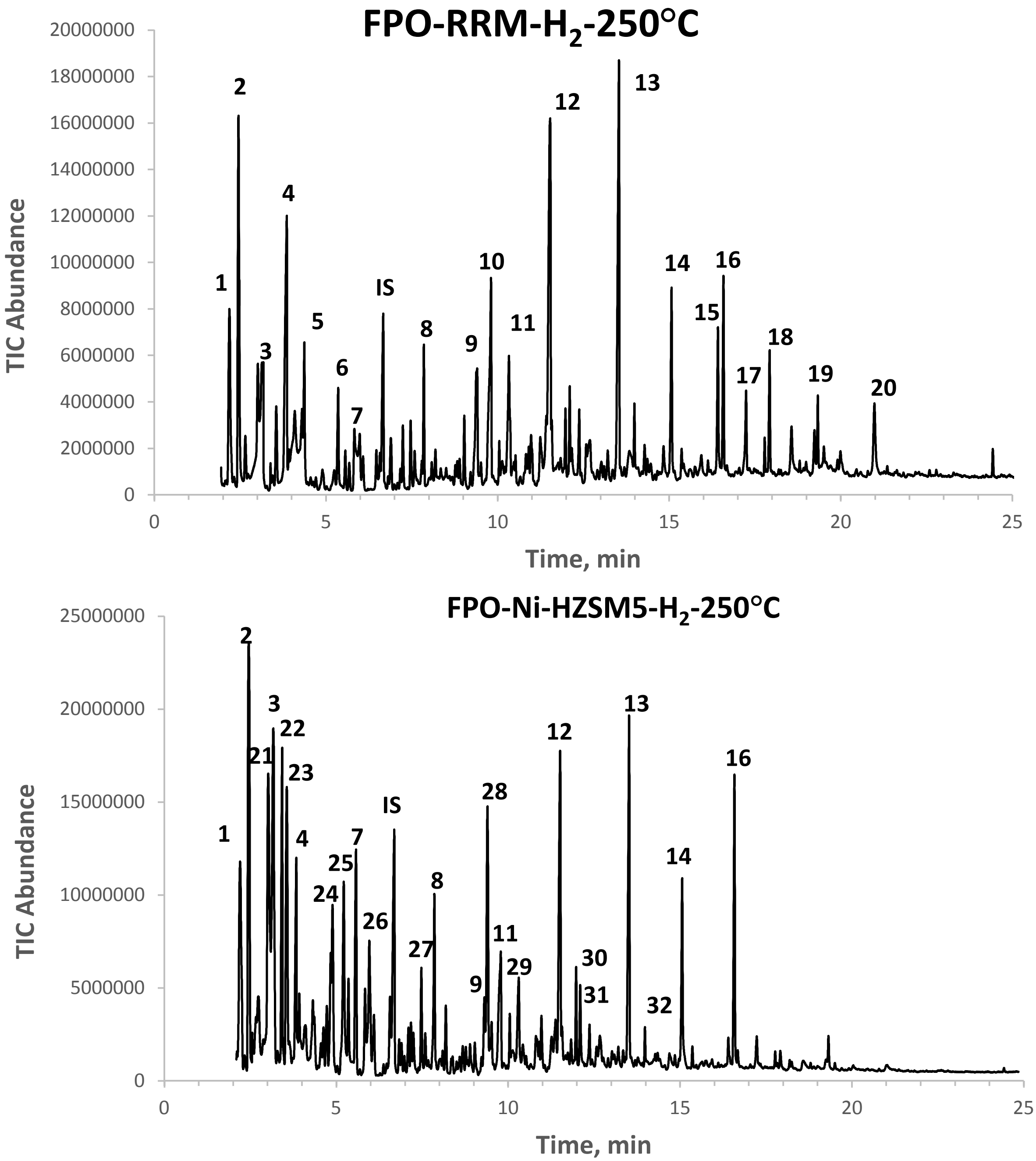


Figure 10S: GC/MS analysis of product from catalytic esterification and hydrogenation (H_2) using RRM and Ni-HZSM-5 of a FPO feedstock (50/50 mixture of oil and methanol) with a solvent delay. (1) ethane, 1,1-dimethoxy-, (2) methyl propionate, (3) acetic acid, (4) Glycolic acid, methyl ester, (5) lactic acid, methyl ester, (6) Glycolaldehyde dimethyl acetal, (7) Pentanoic acid, methyl ester, (IS) Hexanol, (8) Hexanoic acid, methyl ester, (9) Pentanoic acid, 4-oxo-, methyl ester, (10) Propanoic acid, 2-methyl-, anhydride, (11) Butanedioic acid, dimethyl ester, (12) Phenol, 2-methoxy-, (13) Phenol, 2-methoxy-4-methyl-, (14) Phenol, 4-ethyl-2-methoxy-, (15) Eugenol, (16) Phenol, 2-methoxy-4-propyl-, (17) Naphthalene, 1,3-dimethyl-, (18) Phenol, 2-methoxy-4-(1-propenyl)-, (19) Nonanedioic acid, dimethyl ester, (20) Benzeneacetic acid, 4-hydroxy-3-methoxy-, (21) Propane, 1,1-dimethoxy-, (22) 2-Propanone, 1-hydroxy-, (23) Butanoic acid, methyl ester, (24) cyclopentanone, (25) Ethane, 1,1,2-trimethoxy-, (26) Cyclopentanone, 2-methyl, (27) 2-methyl-2-Cyclopenten-1-one, (28) 2-methyl-Benzene, 1,2,4-trimethyl-, (29) Heptanoic acid, methyl ester, (30) Octanoic acid, methyl ester, (31) Pentanedioic acid, dimethyl ester, (32) Nonanoic acid, methyl ester.

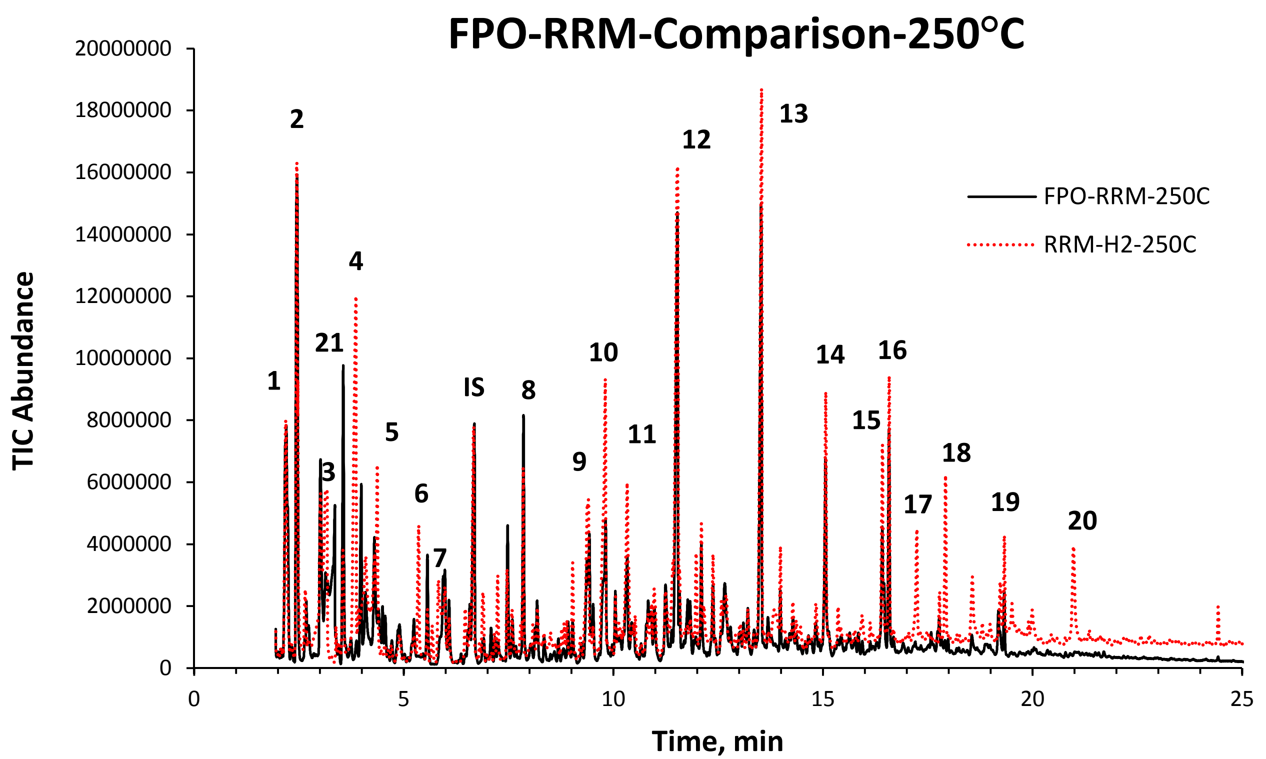


Figure 11S: Overlay of GC/MS analysis of products from catalytic esterification (black trace) and hydrogenation (red trace) using RRM (50/50 mixture of oil and methanol) with a solvent delay. (1) ethane, 1,1-dimethoxy-, (2) methyl propionate, (3) acetic acid, (4) Glycolic acid, methyl ester, (5) lactic acid, methyl ester, (6) Glycolaldehyde dimethyl acetal, (7) Pentanoic acid, methyl ester, (IS) Hexanol, (8) Hexanoic acid, methyl ester, (9) Pentanoic acid, 4-oxo-, methyl ester, (10) Propanoic acid, 2-methyl-, anhydride, (11) Butanedioic acid, dimethyl ester, (12) Phenol, 2-methoxy-, (13) Phenol, 2-methoxy-4-methyl-, (14) Phenol, 4-ethyl-2-methoxy-, (15) Eugenol, (16) Phenol, 2-methoxy-4-propyl-, (17) Naphthalene, 1,3-dimethyl-, (18) Phenol, 2-methoxy-4-(1-propenyl)-, (19) Nonanedioic acid, dimethyl ester, (20) Benzeneacetic acid, 4-hydroxy-3-methoxy-, (21) Butanoic acid, methyl ester.

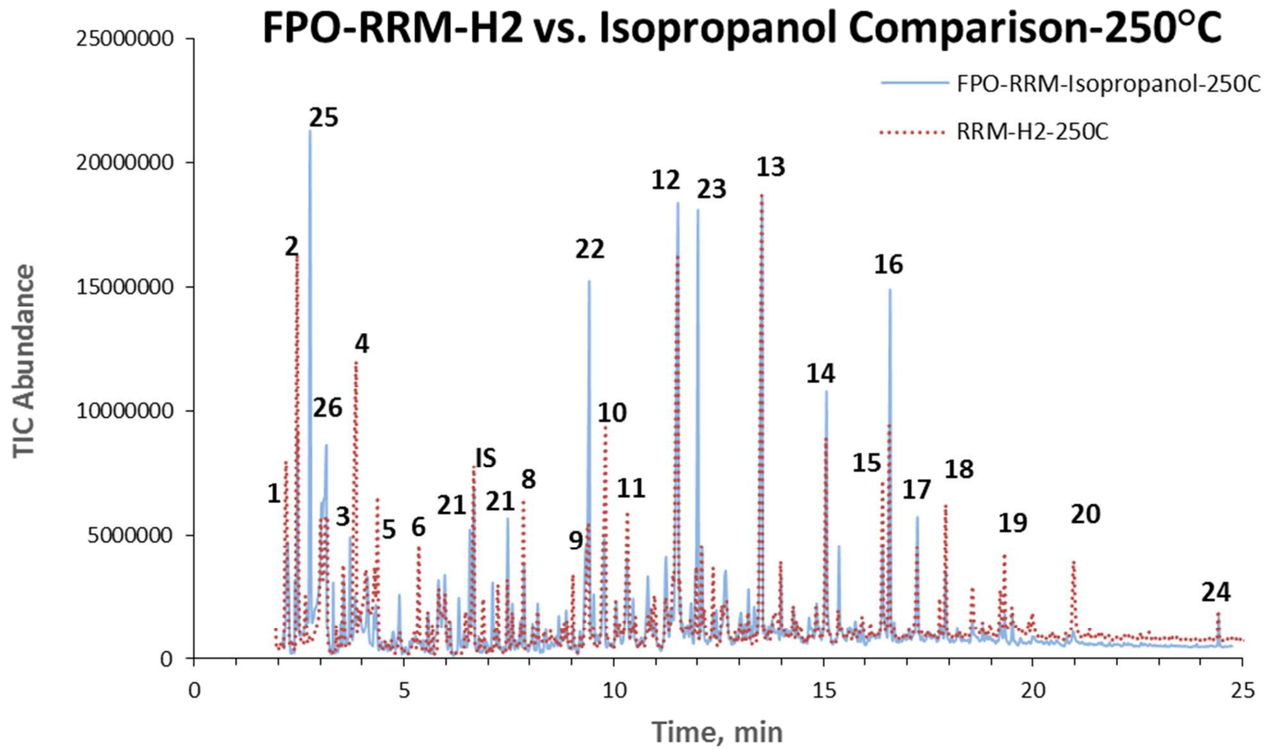


Figure 12S: Overlay of GC/MS analysis of products from catalytic esterification (black trace) and hydrogenation (red trace) using RRM (50/50 mixture of oil and methanol) versus RRM with methanol/isopropanol mixture, with a solvent delay. (1) ethane, 1,1-dimethoxy-, (2) methyl propionate, (3) acetic acid, (4) Glycolic acid, methyl ester, (5) lactic acid, methyl ester, (6) Glycolaldehyde dimethyl acetal, (IS) Hexanol, (8) Hexanoic acid, methyl ester, (9) Phenol, (10) Propanoic acid, 2-methyl-, anhydride, (11) Butanedioic acid, dimethyl ester, (12) Phenol, 2-methoxy-, (13) Phenol, 2-methoxy-4-methyl-, (14) Phenol, 4-ethyl-2-methoxy-, (15) Eugenol, (16) Phenol, 2-methoxy-4-propyl-, (17) Naphthalene, 1,3-dimethyl-, (18) Phenol, 2-methoxy-4-(1-propenyl)-, (19) Nonanedioic acid, dimethyl ester, (20) Benzeneacetic acid, 4-hydroxy-3-methoxy-, (21) p-Xylene or o-Xylene, (22) Benzene, 1-ethyl-3-methyl-, (23) Benzene, 1,2,4,5-tetramethyl-, (24) Pentadecanoic acid, 14-methyl-, methyl ester, (25) Acetic acid, 1-methylethyl ester, (26) Formic acid.