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CYPRUS 2016

Measurement and analysis of tar compounds from thermal valorization of food waste

S. Vakalis, A. Sotiropoulos, K. Moustakas, D. Malamis, F. Patuzzi, M. Baratieri

Limassol, June 25th 2016

Background

- Household waste were sampled, dried and thermally treated for the production of carbonaceous fuels.
- Gaseous products from thermal treatment of biomass contain amounts of tar compounds.

Tar - heavy organic compounds

Tar consists from condensable organic hydrocarbons with a molecular weight bigger than benzene [Neeft et al, 1999]

Background (2)

- Pyrolysis gases are utilized for energy recovery
- Tar compounds cause clogging of the filters, the pipelines and the cylinders of internal combustion engines.
- Until now, there is a lack of technical standards for onsite sampling and for analyzing tar compounds.
  - In particular, tar sampling from raw gas encounters several difficulties.
- In addition, there is not a standarized approach for quantification of tar compounds
  - "In most forms of mass spectrometry, the intensity of ion current measured by the spectrometer does not accurately represent relative abundance, but correlates loosely with it. Therefore it is common to label the *y*-axis with arbitrary units".

Scope

- PAHs are a big fraction of the total tars and the paramount reason of pipes/ engines clogging and corrosion.
- Naphthalene tends to be the dominant tar compound in higher temperatures (Mitchel et al., 2011 and Prando et al., 2016)
- The scope is to accurately sample and quantify naphthalene from **raw gas** of thermal treatment of food waste.

Sampling of food waste and drying

- Household biowaste were sampled and dried in a commercial dryer.
- The structure and the inherent characteristics of organic municipal waste makes the implementation of thermal processes a difficult task.
- Common problems: high moisture & ash, particle size, inhomogenious
- Through efficient dehydration and milling, thermal processes become possible

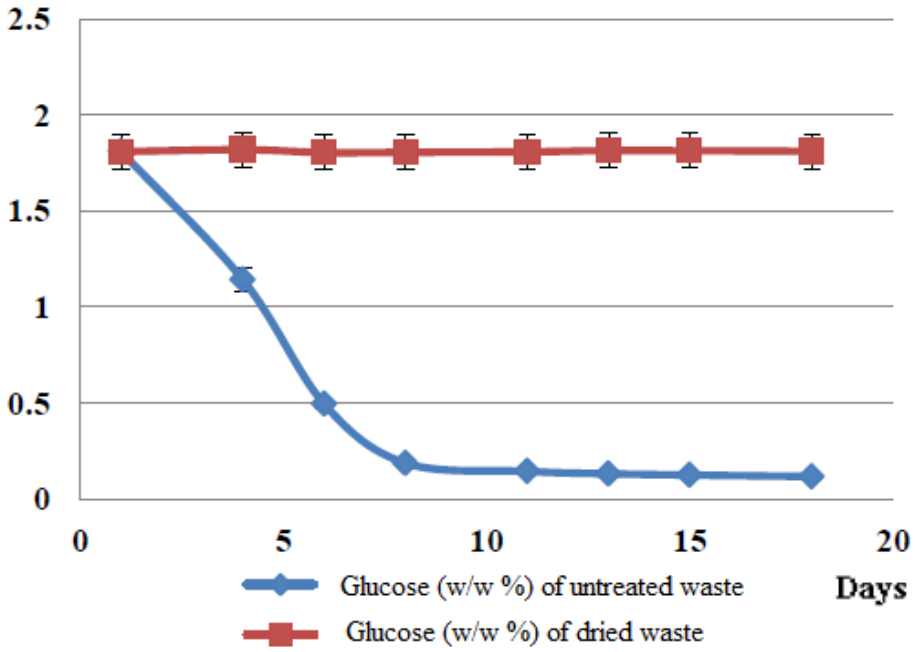
Benefits of drying household waste

Avg. moisture of HW
75% - 95%

70% reduction

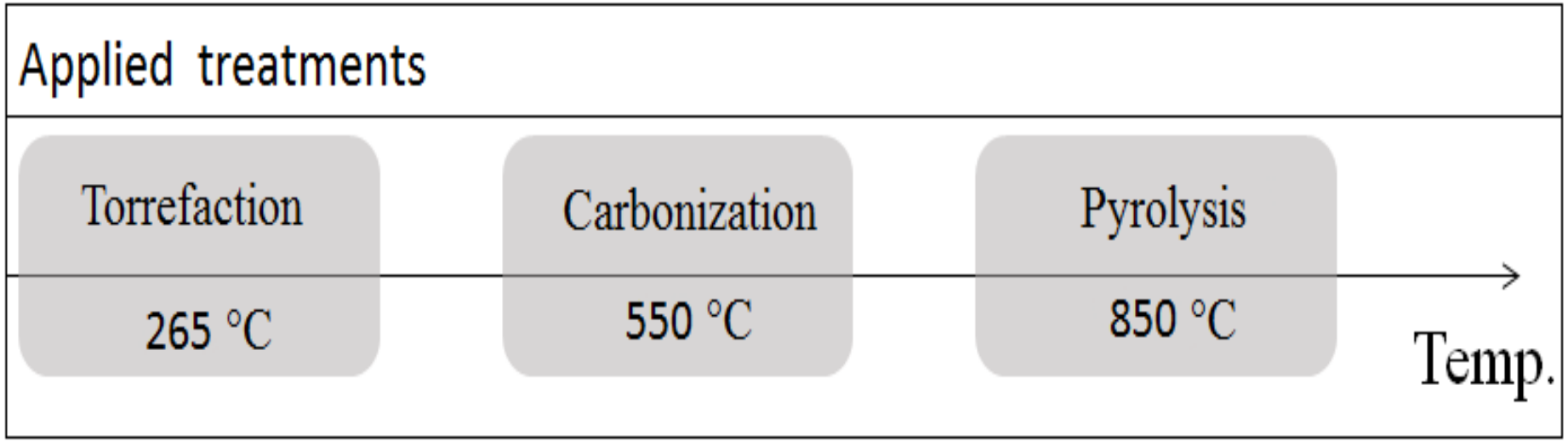
Avg. moisture of dried HW
7%

Also glucose level stays (relatively) stable !



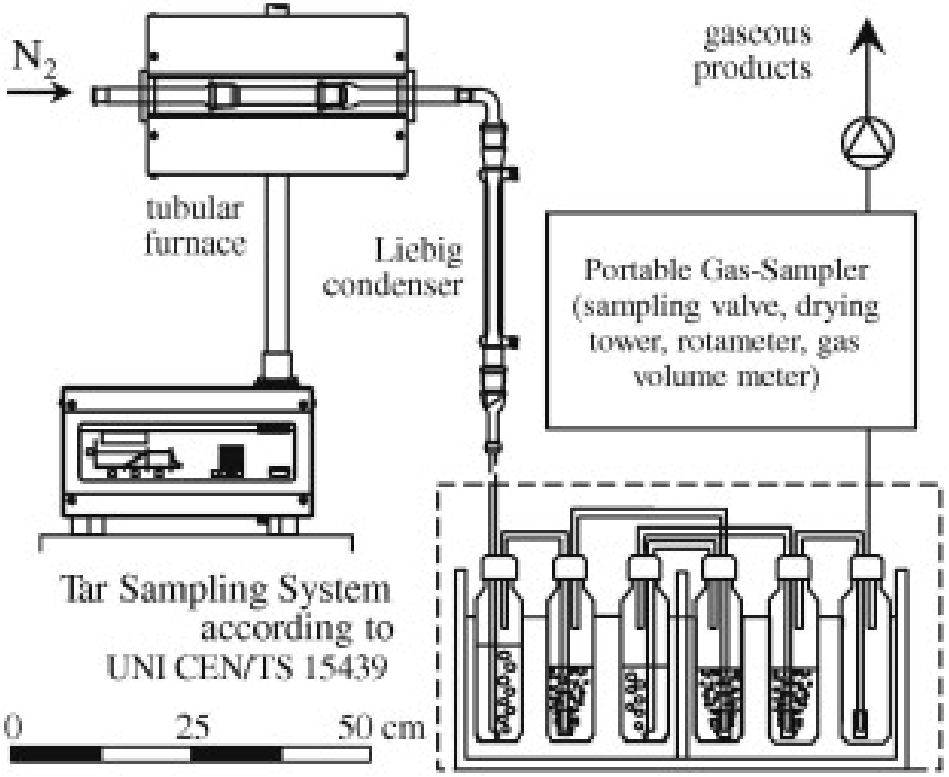
Source: Sotiropoulos A., Malamis D., Loizidou M., (2015). Dehydration of Domestic Food Waste at Source as an Alternative Approach for Food Waste Management. Waste and Biomass Valorization, ISSN 1877-2641, pp6:167-176

Utilization of Thermal Conversion Processes



Source: S. Vakalis, A. Sotiropoulos, K. Moustakas, D. Malamis, K. Vekkos, M. Baratieri. (2016). Thermochemical valorization and characterization of household bio-waste. Journal of Environmental Management.

Scheme of process and products

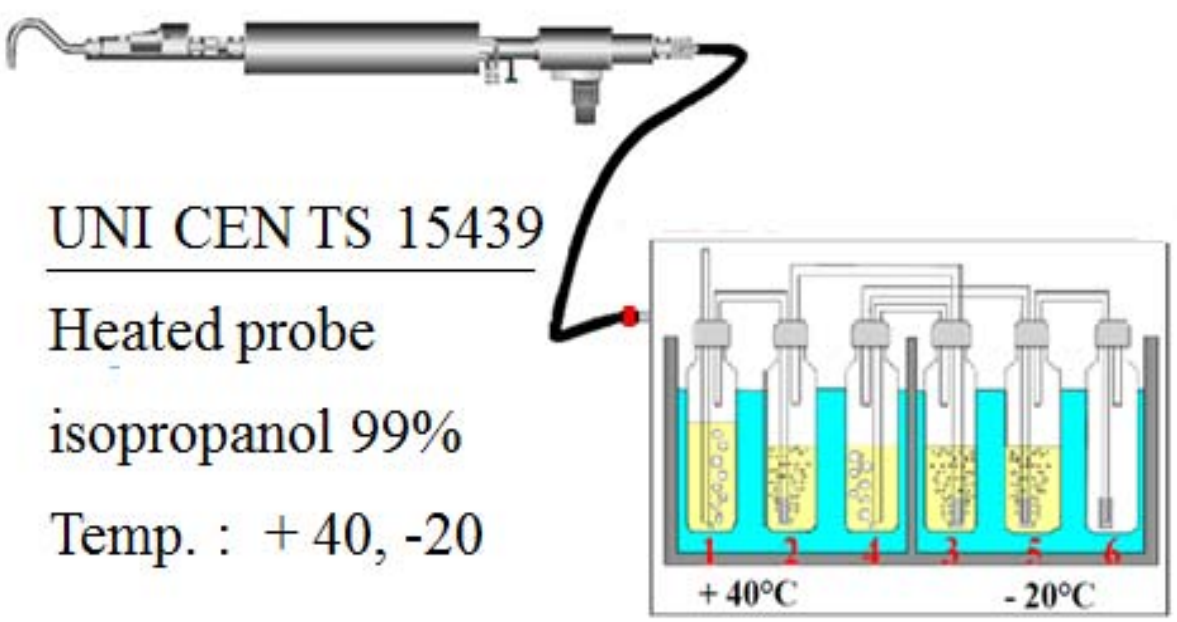


Elemental Analysis of Solid Fractions

	Dried HW	Torrefaction 265 °C	Carb. 550 °C	High T Pyrolysis 850 °C
% wb				
C	42.56	54.96	42.07	53.54
H	6.10	5.01	1.05	1.10
N	1.76	2.43	1.84	1.88
Ash	14	27.85	36.23	37.14
H_2O	7	-	-	-

Source: S. Vakalis, A. Sotiropoulos, K. Moustakas, D. Malamis, K. Vekkos, M. Baratieri. (2016). Thermochemical valorization and characterization of household bio-waste. Journal of Environmental Management.

Tar sampling



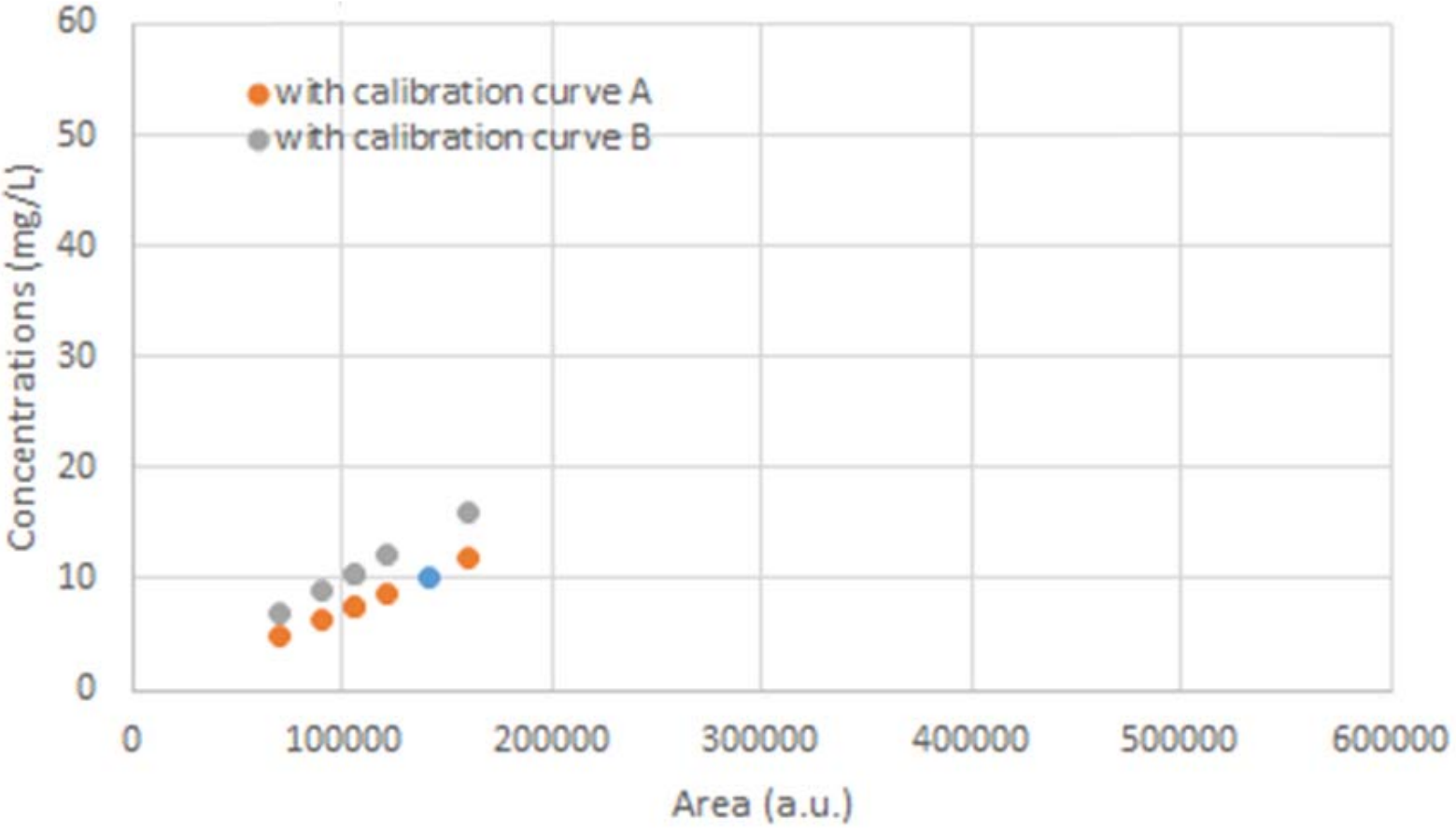
The application of the tar protocol is becoming a standardized approach for gasification systems. But several issues have to be taken into consideration for raw gas sampling and the protocol should be expanded to include other thermal treatment methods.

Source: J.P.A. Neeft, H.A.M. Knoef, P. Onaji , (1999). Behavior of tars in biomass gasification systems. Maarn , The Netherlands

Analysis of tar compounds

- GC- MS unit (Agilent 5977A).
- Addition of a specialized column for tar analysis.
- Identification of retention times for selected tar compounds
- Calibration of the instrument by means of solutions with different naphthalene concentrations.
- Calibration for tar cracking

Developement of calibration curves

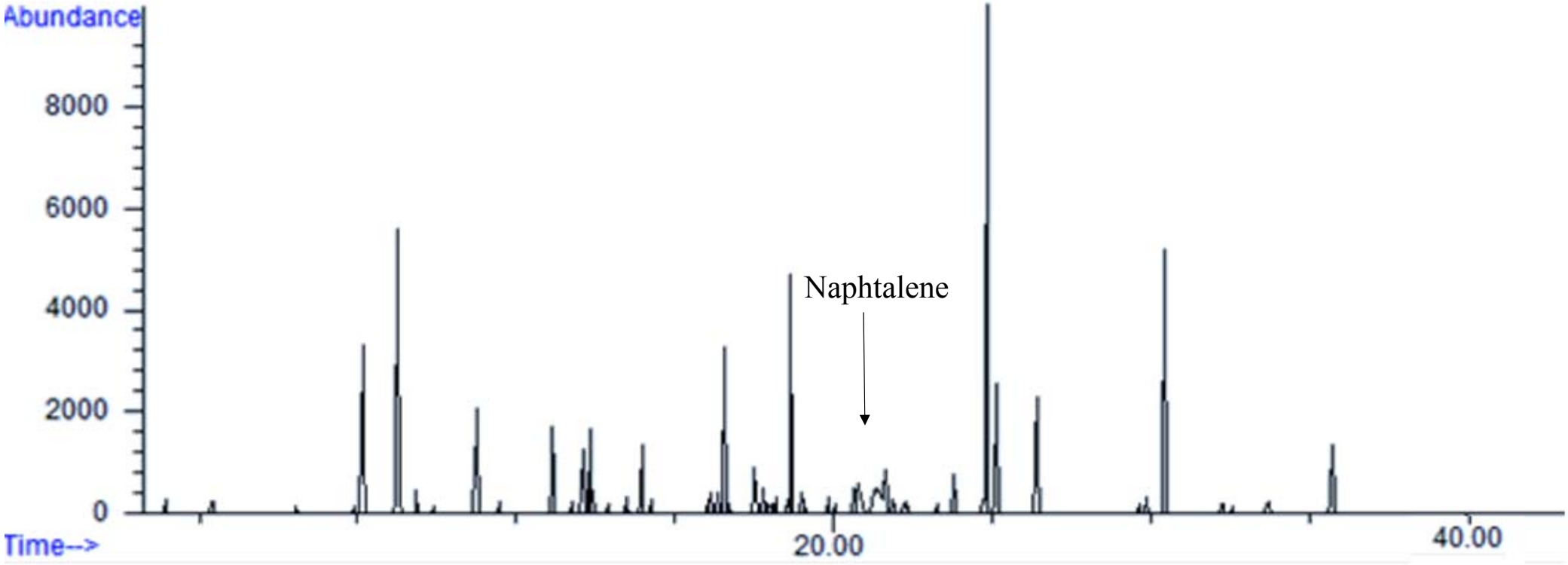


Identification of retention times (GC column)

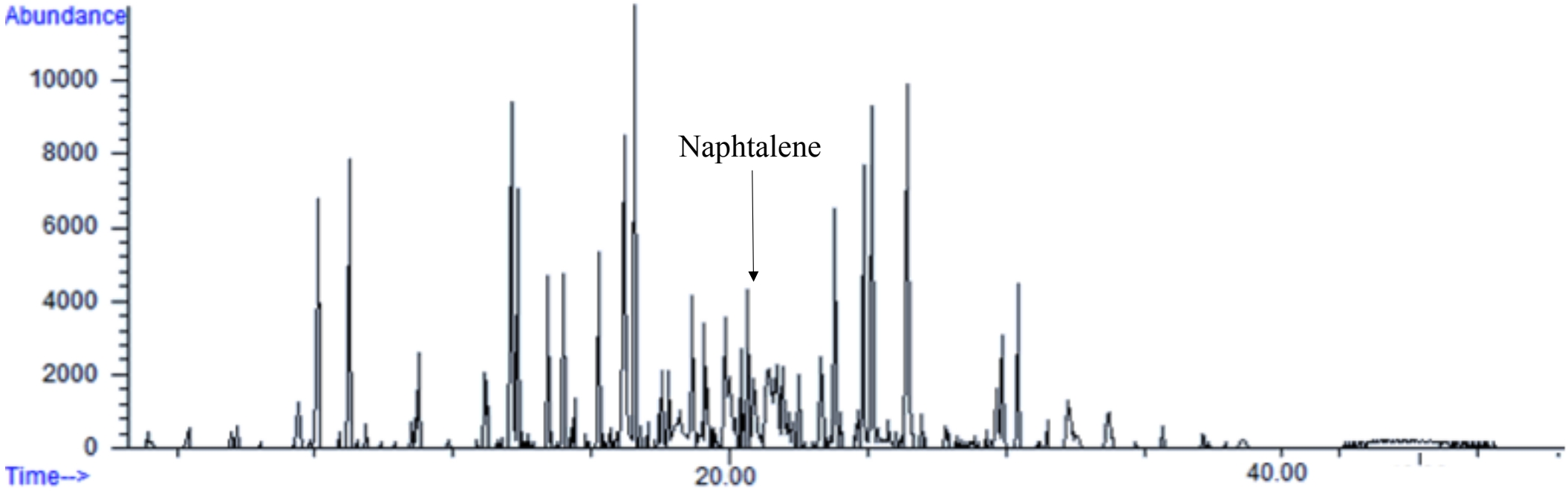
Species with RT less than 20s	
Benzene	3.179
Toluene	5.544
Pyridine, 3-methyl-	7.575
Pyridine, 2-methyl-	9.214
Styrene	10.253
Benzonitrile	13.768
Benzofuran	14.137
Indene	15.837
Benzonitrile, 2-methyl-	16.624
Benzonitrile, 4-methyl-	17.404

Species with RT more than 20s	
Naphthalene	20.509
Benzo[c]thiopene	20.683
Quinoline	22.044
Isoquinoline	22.729
Indole & Naphthalene, 2-methyl	23.737
Naphthalene, 1-methyl	24.164
Biphenyl	26.052
Naphthalene, 2-ethenyl-	27.423
Acenaphthylene	27.94
2-Naphthalenecarbonitrile	29.058

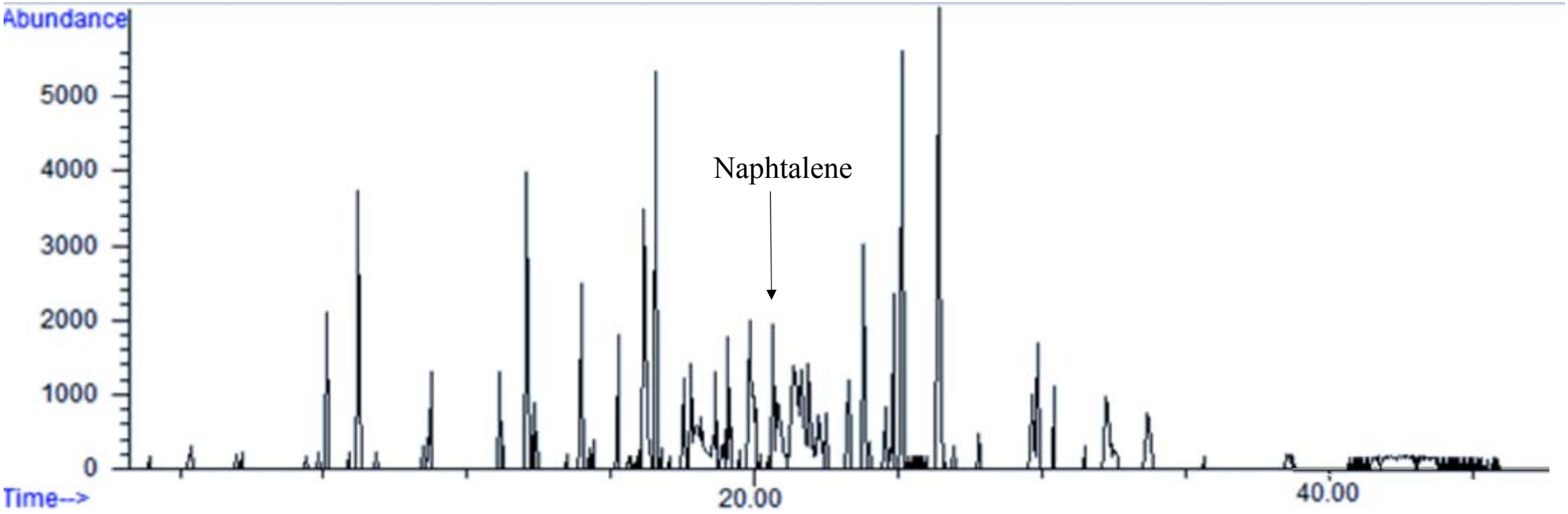
Results: GC-MS Torrefaction



Results: GC-MS Carbonization



Results: GC-MS HT Pyrolysis/ Gasification



Results: naphthalene quantification

	Torrefaction	Carbonization	High T Pyrolysis
	-Naphthalene concentrations (mg/ Nm^3)-		
Curve A	6.32	12.04	7.49
Curve B	8.92	15.95	10.58

Discussion and Conclusions

- A tar sampling standard for all the onsite thermal treatment facilities should be developed.
- Improvements in the existing methods should accomodate the sampling of tar from raw gas.
  - In our case, lab scale operation prevented common problems
- Char enhances the cracking of naphtalene.Thus, napthalene in high T Pyrolysis gases has smaller concentrations than Carbonization.
- Other species were identified like Indene, Pyridine and Biphenyl but their quantification will be presented in future publications.

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THANK YOU FOR YOUR ATTENTION!

For further info:

stergios.vakalis@outlook.com