Pyrolysis characteristics of discarded fishing net collected from Gulf of Thailand using Py-GCMS

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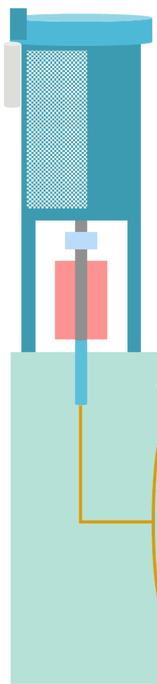
Abandoned, lost or otherwise discarded fishing gear (ALDFG) is a serious growing concern globally due to its numerous critical impacts on environment and economic [1]. Therefore, a number of international organizations have been keen about the activities and agreements on resolving marine debris crisis. In general, good condition fishing nets, particularly those end-of-life gears, could further be upcycled to carpet tiles and the likes. In case of polymer recycling, they would be melted and molded into various components [2]. However, some fishing net wastes are not suitable for upcycling, even mechanical recycling due to their inherent mixed and heterogeneous materials, they could be thermally transformed as a feed stock recycling. Pyrolysis is one of the major applied thermal processes which could break down mixed polymers and impurities in plastic fraction into base monomers [3]. Therefore, thermochemical conversion is prospective technique to overcome the limitation of mixed-material [4] which is unique to most fishing net wastes [5] including non-polymer material from the production line, e.g. heavy metals. In addition, this type of waste could be contaminated during their usage such as the fishing gears that were soaked in seawater for a long time. Since most of fishing gears production rely on petroleum-based raw materials, their derivatives from thermochemical processes would be the major products which can be further utilized as feedstock for petroleum-based manufacture [7]. For example, if chemical yields is monomer species, the interesting value-added pathway might be recaptured and applied as the petroleum-based chemical or fuels. The main route for fuel and chemical production from plastic waste is the pyrolysis process [6], for instance, HDPE fishing net waste could be recovery as liquid fuel by this process [7].

The Gulf of Thailand (GoT) is located in Southeast Asia surrounded by Cambodia, Malaysia, Vietnam, and Thailand. In recent years, unfortunate news of large derelict fishing nets covering the massive area of the plentiful coral reef had stunned the public due to the dimension and coverage area of this ghost net of 200 meter in length and 50 meter in width, and weight of 0.8 tons. Soon after, there were a few derelict fishing nets which covered around 400 m^2 of sea floor and coral reef retrieved from seafloor of GoT. Those were collected by specialist drivers from government agencies and volunteers. This research investigates four derelict fishing nets from those retrieving. To aid establishing of relevant regulations and enable more appropriate, effective, and environmentally sound recycling and recovery, characteristics of collected discarded fishing net (FN) and released contaminant data during thermal decomposition are collected in this study.

Discarded fishing net (FN)

- *FN or "Ghost net" can entangle marine life.*
- *FN were collected from 4 locations of GoT noted as **KFN**, **LFN**, **MFN**, and **UFN***
- *Collected by specialist driver from government agencies and volunteer.*



Pyrolyzer

Pyrolysis temperature; 400-700 °C

Sprit ratio; 1:200

GC column; Agilent UA-5

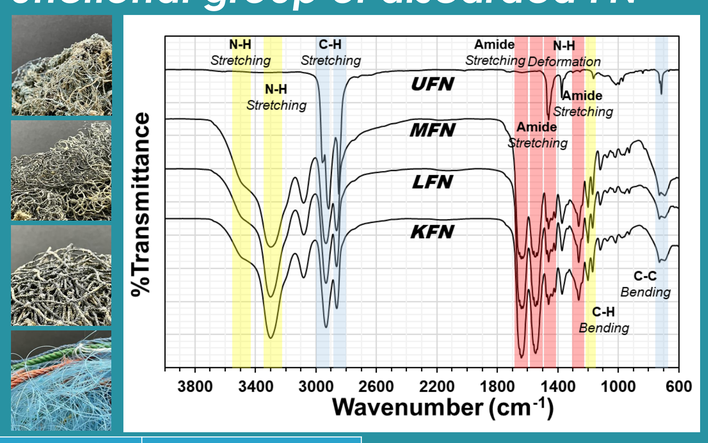
Analysis

1	*Chemical species released from discarded FN*
2	*Distribution of release compound*
3	*Focusing on monomer species for further promising pathway*
4	*Information for further liquid fuel and its upgrading process.*

Synthetic polymer fishing net (FN)
- ***Polyamide: KFN / LFN / MFN***
- ***Polyolefins: UFN***

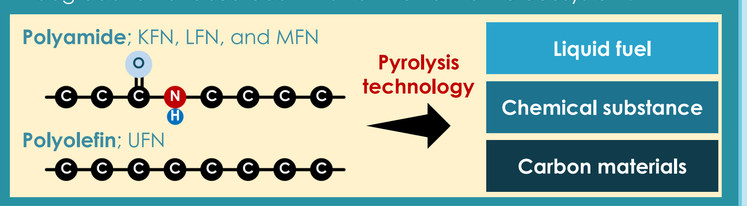
Results and discussion

Functional group of discarded FN

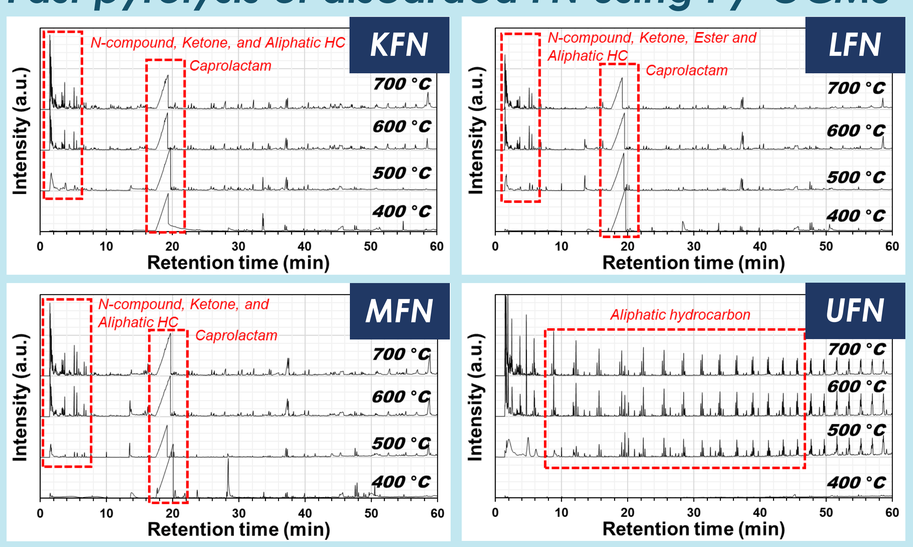


Wavenumber (cm^{-1})	Assignment
3400	N-H stretching
3300	N-H stretching
3100-2800	C-H stretching
1636	Amide stretching
1548	Amide stretching
1460	Amide deformation
1264	Amide stretching
1200	C-H bending
690	C-C bending

- Regarding on FTIR spectrogram, discarded FNs collected from GoT are mainly categorized into 2 types of synthetic polymer, **Polyamide or Nylon** (KFN, LFN, and MFN) and **Polyolefins** (UFN)
- Many additives are added during the processing of polyamide and polyolefin , for example, antioxidant, chain extender, processing aids, and heat stabilizer.
- Releasing of these additives and monomer to the seawater from degradation of discarded FN is harmful to marine ecosystem.



Fast pyrolysis of discarded FN using Py-GCMS

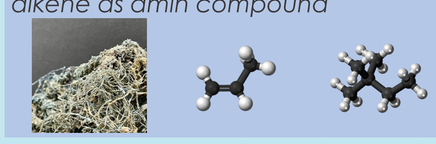


Polyamide type FN

***Caprolactam** as monomer of Nylon 6 as main compound*

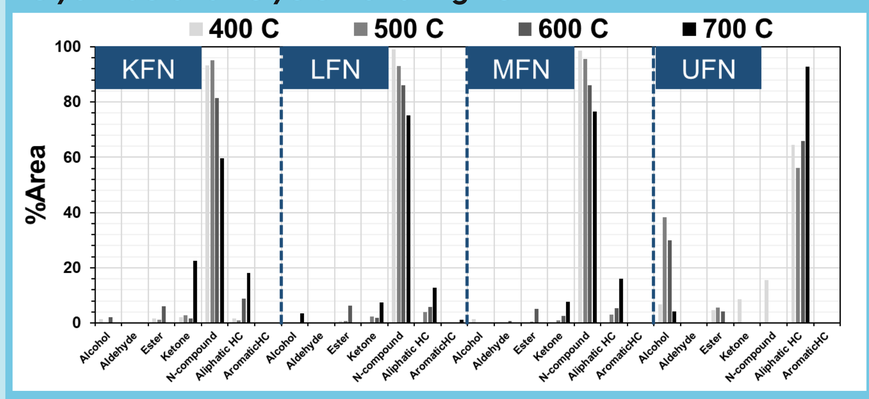
Polyolefin type FN

***Aliphatic hydrocarbon** as alkane and alkene as amin compound*



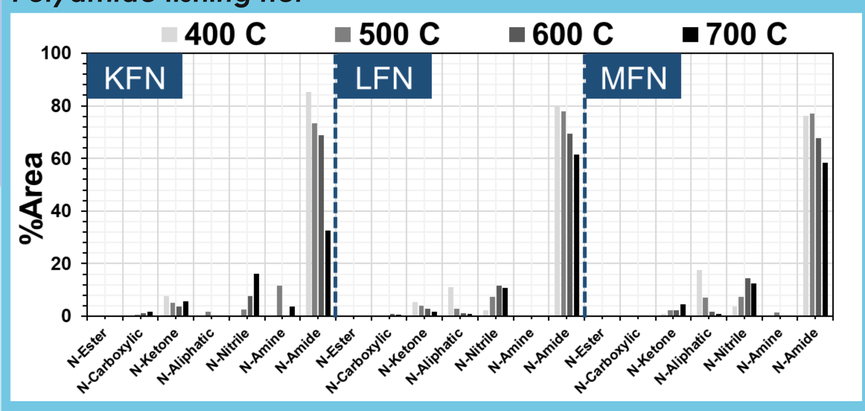
- GC chromatograms of 4 discarded FN (KFN, LFN, MFN, and UFN) at various pyrolysis temperature (400, 500, 600, and 700 °C) exhibited characteristic of polyamide (KFN, LFN, and MFN) and polyolefin (UFN) which corresponded well to FTIR spectrogram.
- For polyamide type FN (KFN, LFN, and MFN), **Caprolactam**, a monomer, was observed as major signal at any pyrolysis temperatures around RT 17-20 min. and N-compounds were also presented along with minor Ketone and Aliphatic HCs.
- For polyolefin type FN (UFN), **Aliphatic HCs** were mainly detected with equally interval RT during pyrolysis at 500-700 °C while 400 °C is too low for C-C chain fragmentation. Unfavorable oxygenated compounds, Alcohol and Ester, were presented at these conditions as well.

Polyamide and Polyolefins fishing net



- Polyamide (KFN, LFN, and MFN), depropagation of Nylon 6 results in **N-compound as major pyrolysis products at 400 °C (93-98%)** with tendency to reduce at higher temperature and results in Aliphatic HC and O-containing compounds (Ketone and Ester).
- Polyolefins (UFN), **64 % of product selectivity is Aliphatic HC** at 400 °C and significantly raised to 92% at 700 °C, resulting from random chain scission of polymer backbone.

Polyamide fishing net



- Pyrolysis vapor from Polyamide FN is mainly N-compounds, Amide functional groups (32-85%), and tend to thermally reduce at 700 °C.
- Reduction of Amide compound by decarbonylation results in drastically increased of nitrile compound from 2-3% (400 °C) to 10-16% (700 °C).

Summary

- **Discarded FNs collected from GoT are mainly categorized into 2 types of synthetic polymer, Polyamide (KFN, LFN, and MFN) and Polyolefins (UFN).**
- **Caprolactam, a monomer, was observed as major product from degradation of Polyamide type FN with N-compound 60-98%.**
- **Pyrolysis vapor from Polyamide FN is mainly N-compounds, Amide functional groups (32-85%), and tend to thermally reduce at 700 °C.**
- **Aliphatic HCs, was observed as major product from degradation of Polyolefins type FN with 64-92%.**
- **Difference on product selectivity between Polyamide and Polyolefin FN is due to its instinctive depolymerization mechanism with depropagation and random chain scission, respectively.**

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