NANYANG TECHNOLOGICAL UNIVERSITY SINGAPORE

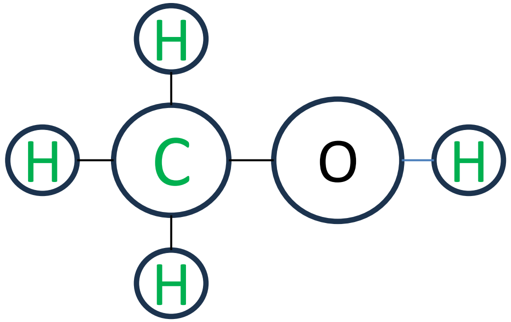
Methanol – Fuel Assurance and Fingerprinting

Keat Ping YEOH
Research Fellow
Maritime Energy & Sustainable Development Centre of Excellence (MESD)

Nov 7, 2024

Agenda

- Introduction and Motivation



- Methanol Production Pathways
- Radiocarbon Measurement to Determine Biogenic Content
- Ongoing Developments and Future Work

Decarbonisation of the Maritime Sector

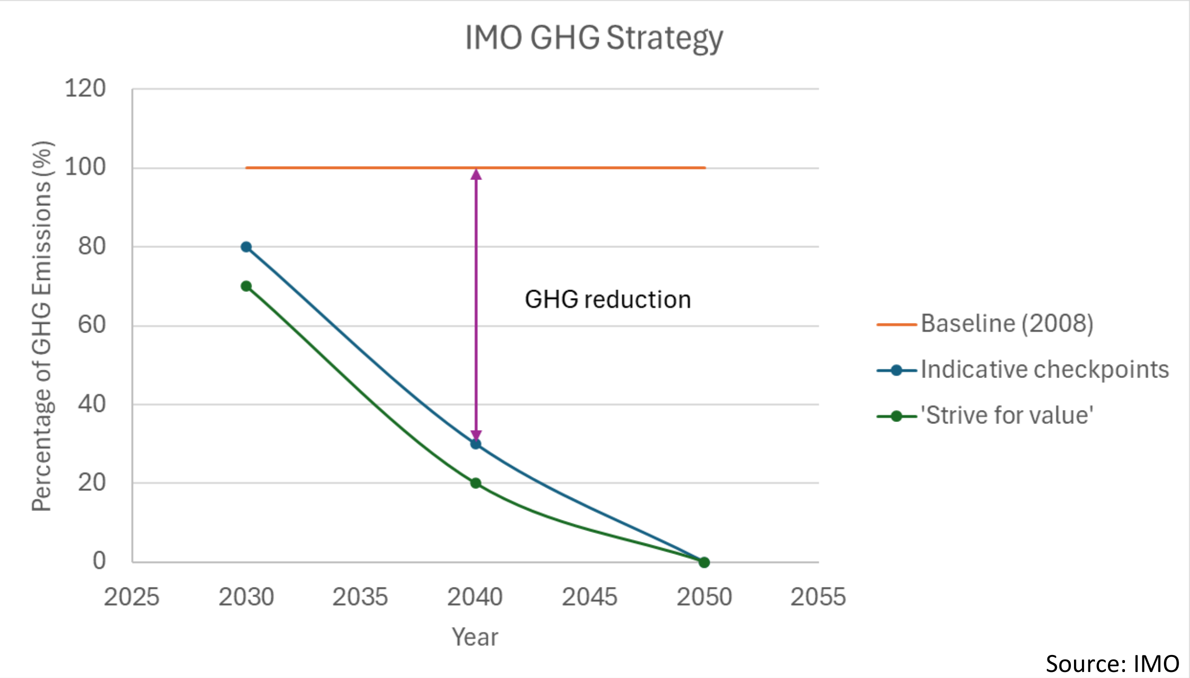


Figure 1: International Maritime Organization (IMO) greenhouse gas (GHG) emission reduction strategy

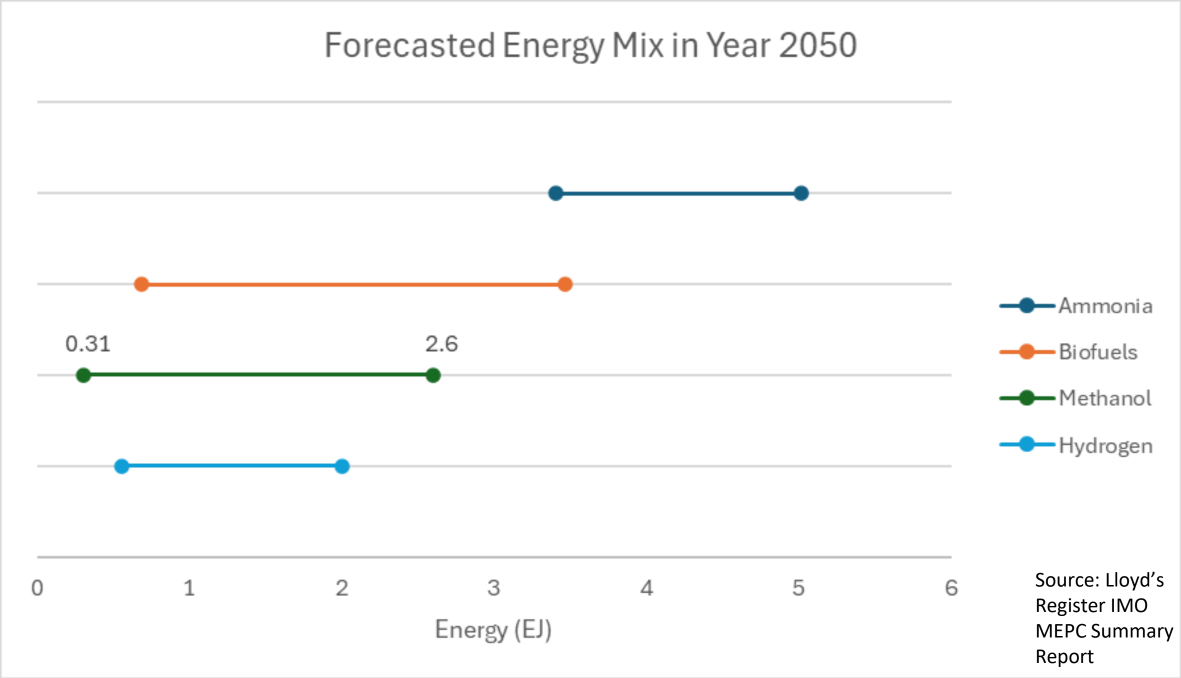


Figure 2: Forecasted energy contribution range of marine fuels in 2050 (1 EJ = 10^{18} J or 10^{12} MJ)

Methanol is a promising marine fuel to aid in decarbonising the maritime sector.

Role of Certification Schemes in Decarbonisation

- IMO currently accepts biofuels certified by the following sustainable certification scheme providers*:
  - International Sustainability and Carbon Certification (ISCC)
  - Roundtable on Sustainable Biomaterials (RSB)

ISCC International Sustainability & Carbon Certification

RSB®

* Source: MEPC.1/Circ.905

Role of Certification Schemes in Decarbonisation

- Feedstock identification: type and sustainability
- On-site audits
- Usage of mass balance calculations and attribution approaches
- GHG intensity calculations (actual and default values)
- Traceability: Proof of sustainability document

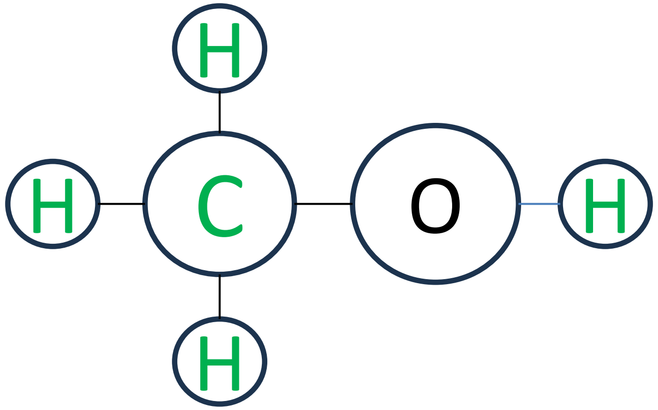
Source: ISCC – Introduction to ISCC

Methanol Fuel Assurance and Fingerprinting

Feedstock identification: type and sustainability

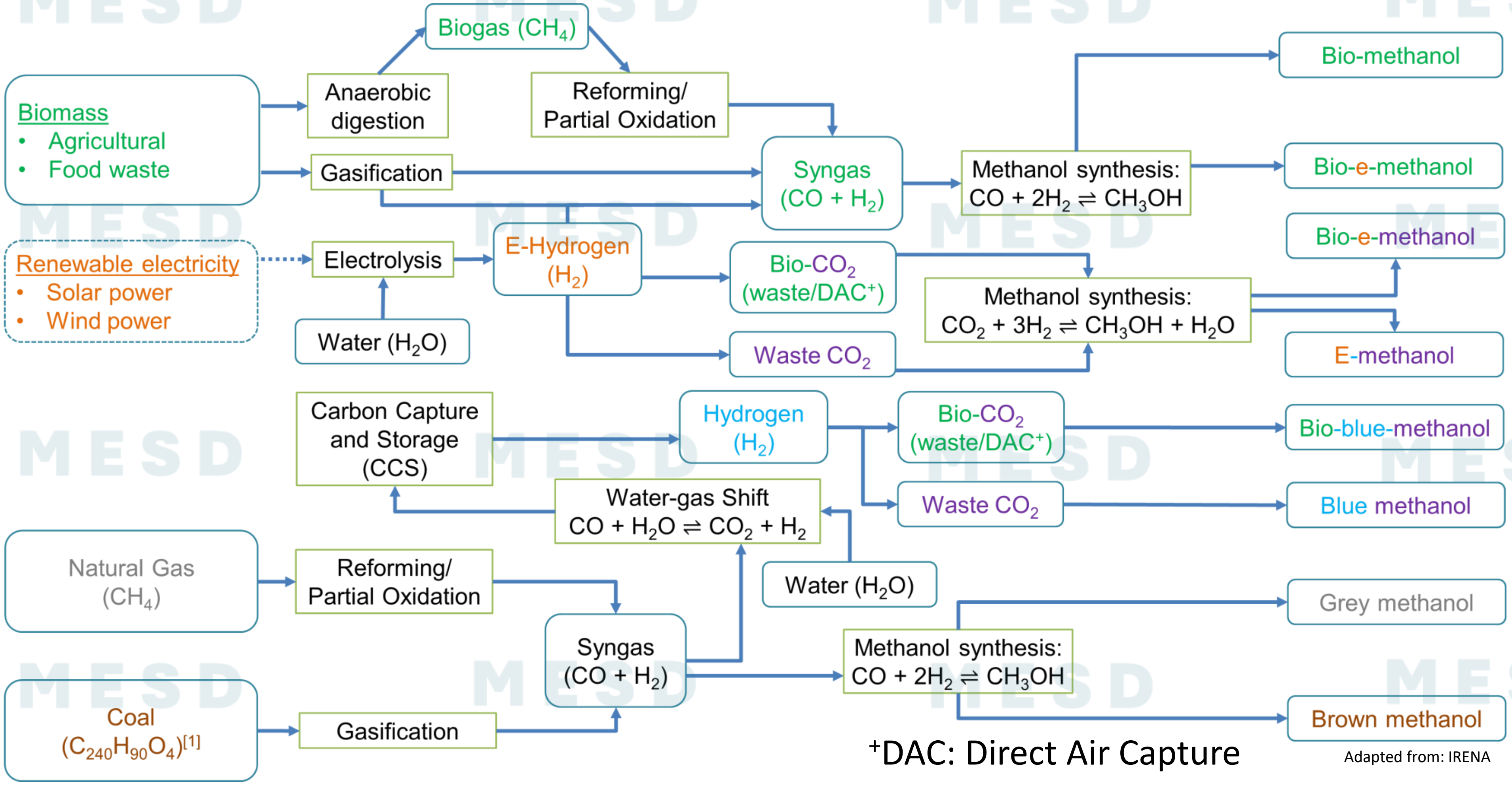
Traceability: Proof of sustainability document

Other feedstock tracing methods:
- Dosing with tracer
  - DNA, isotope
- Blockchain technology
  - Ensures digital records cannot be tampered with



- Fingerprinting of methanol based on its **intrinsic properties**
- Identify the methanol production **feedstock**
- **Complements** certification schemes and other tracing technology

Methanol Production Pathways



+DAC: Direct Air Capture

Adapted from: IRENA

Emission credits generated by biomass growth*

**may not apply to Bio-CO_2*

Emission credits from captured CO_2 used to produce methanol**

***Currently set at zero pending further methodological guidance*

Emission credits from net CO_2 captured and stored for at least 100 years

Emission credits listed here are based on the IMO MEPC 2024 LCA Guidelines

[1] Petroleum and Coal – Purdue University

Radiocarbon C-14

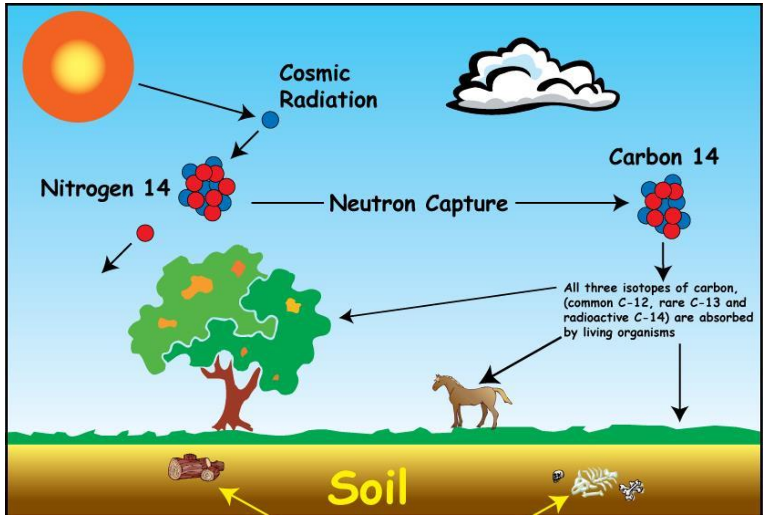


Figure 3: Illustration of C-14 formation in the atmosphere and its uptake by living organisms [1]

- Living organisms absorb C-14
- No new C-14 uptake after death
- Decay of C-14 reduces C-14 content

- Coal and natural gas:
  - Formed > 100 million years ago [2], [3]
- Biomass: < 100 years

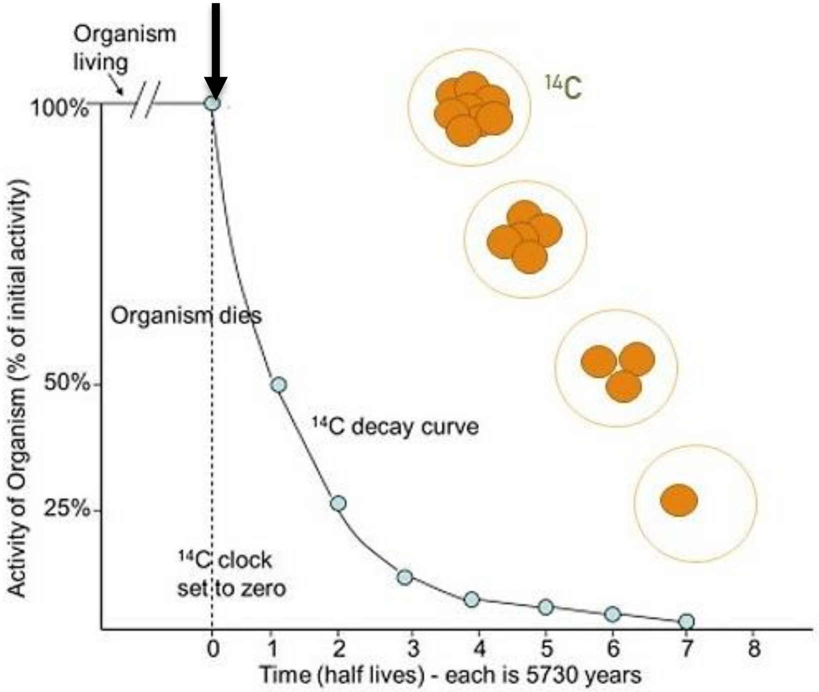
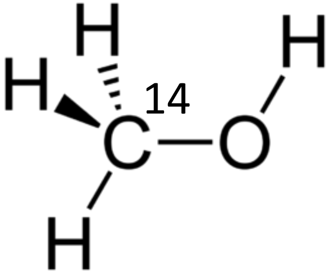
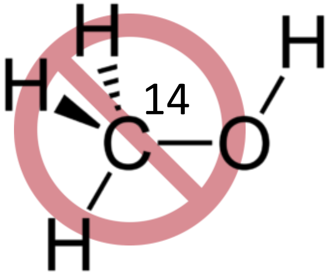


Figure 4: Decay curve of the C-14 isotope [1]

- C-14 detection limit: 43500 years before present [4]



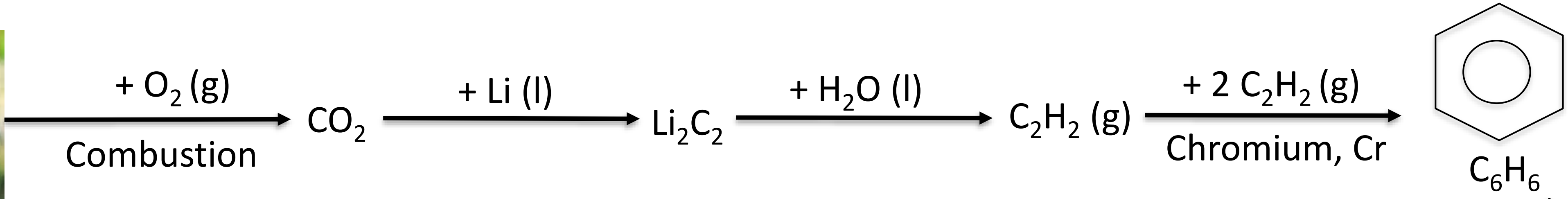
➢ C-14 levels in recent living materials matches atmospheric levels

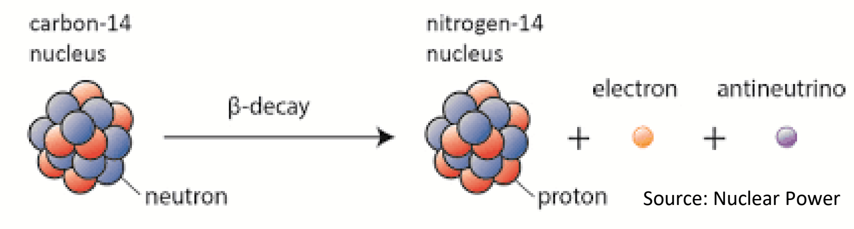


➢ C-14 cannot be detected in fossil fuels

[1] Rlrc, & Rlrc. (2022, August 15). *History & Advances in Radiocarbon Dating - Beta Analytic*. Carbon Dating Service
[2] Coal. (n.d.). National Geographic
[3] How natural gas is formed. (2014, June 19). Union of Concerned Scientists
[4] Beta Analytic. Lab Capacity & Detection Limits.

Liquid Scintillation Counting (LSC)





Source: Nuclear Power

Add scintillation cocktail:
e.g. Butyl-PBD or PPO/POPOP dissolved in toluene

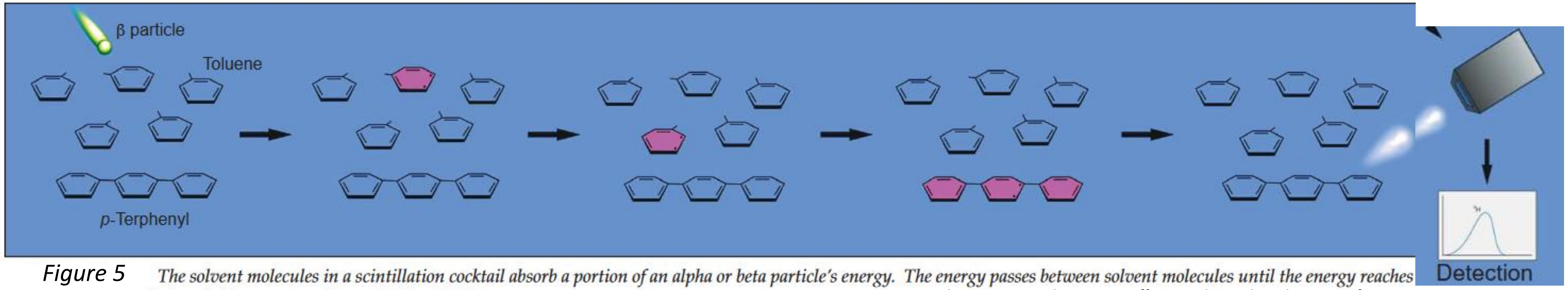


Figure 5 *The solvent molecules in a scintillation cocktail absorb a portion of an alpha or beta particle's energy. The energy passes between solvent molecules until the energy reaches a phosphor, which absorbs the energy and re-emits it as light.*

Source: National Diagnostics Laboratory Staff. Principles and Applications of LSC

LSC measurement relies on the radioactivity from the decay of C-14 atoms

 NANYANG TECHNOLOGICAL UNIVERSITY | SINGAPORE

Confidential

MESD Centre of Excellence

Accelerator Mass Spectrometry (AMS)

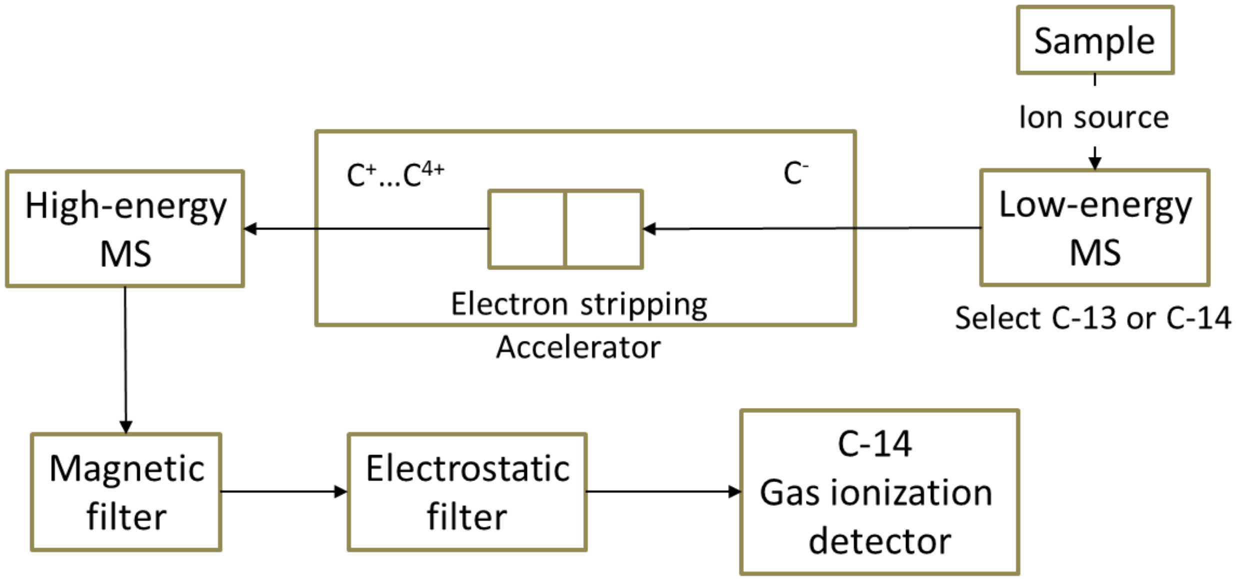


Figure 6: Schematic of an AMS setup

Source: Nnane & Tao (2005). DRUG METABOLISM | Isotope Studies

1. Atoms in the sample are converted into a fast moving ion beam, by bombarding the sample with caesium ions
2. The ions are accelerated and and they collide with the gas molecules in the electron stripping canal, where C^{3+} ions are formed
3. The magnetic filter selects ions with the momentum expected of ^{14}C ions

- AMS measurement relies on the different **mass-to-charge ratio** of carbon isotopes and other atoms

For both LSC and AMS, the results are reported in Percentage Modern Carbon (pMC):

$$\text{pMC} = \frac{C-14\ content\ of\ sample}{C-14\ content\ in\ standard\ reference\ material\ SRM\ 4990B\ (from\ year\ 1950)} \times 100\%$$

C-14 As An Indicator Of Biogenic Content

Table 1: Reported values of Percentage Modern Carbon for biofuel

Biofuel	**Percentage modern carbon/pMC (%)**	**Remarks**
Jet fuel	112.45 ± 0.32	Produced from hydrotreated pine sawdust fast pyrolysis oils obtained from the Technical Research Center of Finland
Hydrotreated pyrolysis oil	89.97	Produced at National Renewable Energy Laboratory
B100 commercial biodiesel	92.4 ± 0.27	-

Source: Lee, J. E., Li, Z. H., Wang, H., Plymale, A. E., & Doll, C. G. (2022). Quantification of biogenic carbon in fuel blends through LSC 14C direct measurement and assessment of uncertainty. Fuel, 315, 122859.

- **ASTM D6866**: Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis
- **ISO 16620-2**: Plastics. Biobased content. Determination of biobased carbon content (equivalent to ASTM D6866)
- **DIN 51637** (German standard) – Biobased Content Testing of Hydrogenated Vegetable Oil (HVO)

➢ percent Modern Carbon **(pMC) value differs** even for pure biofuel: 89.97 – 112.45, 100 pMC ≠ 100% biogenic
➢ The **pMC value range** for pure bio-methanol needs to be determined

Preliminary findings: Radiocarbon content of methanol

Table 2: Radiocarbon content of methanol tested using ASTM D6866 Method B (AMS)

Sample	pMC	Biogenic Carbon Content/%	Methanol Feedstock
Bio-methanol	108.87 ± 0.31	97	Black liquor
60% Bio-methanol	66.10 ± 0.21	66	Mixed
Methanol	0.52 ± 0.05	1	Fossil fuel (natural gas and/or coal)

Sample calculation to convert pMC to Biogenic Carbon Content:

$$108.87 \times \frac{99.7}{112} = 96.9\ \%$$

- **99.7** - Atmospheric adjustment factor in year 2024 (REF)
- **112** - Adjustment factor to account for bomb carbon when **105.7 < pMC < 121.7**
- **Error** (absolute) of biogenic carbon content is **within 3 % tolerance** as cited in ASTM D6866

Source: ASTM D6866-24

Confidential

Preliminary findings: Radiocarbon content of methanol

Table 2: Radiocarbon content of methanol tested using ASTM D6866 Method B (AMS)

Sample	pMC	Biogenic Carbon Content/%	Methanol Feedstock
Bio-methanol	108.87 ± 0.31	97	Black liquor
60% Bio-methanol	66.10 ± 0.21	66	Mixed
Methanol	0.52 ± 0.05	1	Fossil fuel (coal and/or natural gas)

If the bomb carbon **adjustment factor** is applied:

$$66.1 \times \frac{99.7}{112} = \mathbf{58.8}\ \%$$

- ➢ Further **evaluation** on the usage of adjustment factors

- **99.7** - Atmospheric adjustment factor in year 2024 (REF)
- **112** - Adjustment factor to account for bomb carbon when **105.7 < pMC < 121.7**

Source: ASTM D6866-24

Preliminary findings: Radiocarbon content of methanol

Table 2: Radiocarbon content of methanol tested using ASTM D6866 Method B (AMS)

Sample	pMC	Biogenic Carbon Content/%	Methanol Feedstock
Bio-methanol	108.87 ± 0.31	97	Black liquor
60% Bio-methanol	66.10 ± 0.21	66	Mixed
Methanol	0.52 ± 0.05	1	Fossil fuel (coal and/or natural gas)

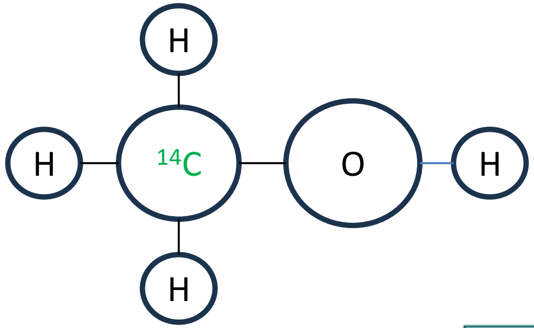
- Negligible amount of radiocarbon present, possibly due to:
  - Renewable natural gas (RNG) injected into the natural gas network
  - Surfactant in coal slurry

Limitations of Radiocarbon Testing

- **Cannot be used** in the identification of methanol made from captured CO_2 from a **non-biogenic source** e.g. blue methanol, e-methanol
- The **type of biomass feedstock** cannot be identified, hindering the assessment of the sustainability of the feedstock used.
- The **energy source** used in the production process cannot be identified
    - ➢ This is also a limitation of methanol fingerprinting

Ongoing Developments and Future Work

- Further **validate and refine** the usage of radiocarbon content testing in methanol fingerprinting



- Identify and quantify the **impurity profile** of methanol produced via different pathways
  - ➢ may be used to differentiate <u>blue, e-methanol</u>

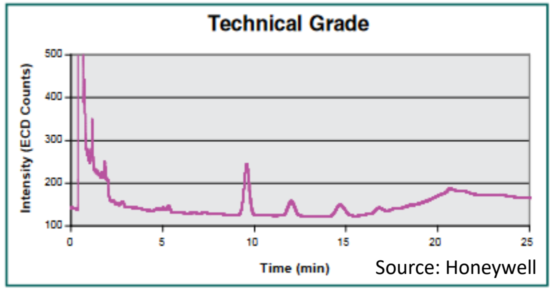


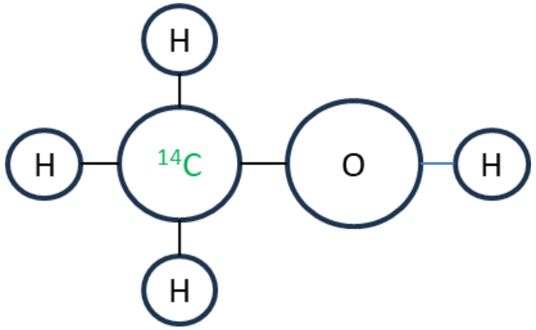
Figure 7: GC results of technical grade methanol

- Develop methods to enhance the **resolution of feedstock identification** beyond the biogenic/non-biogenic classification.

Confidential

Summary and Conclusion

- Methanol as a fuel for **decarbonisation**
- Fingerprinting to **complement** other feedstock tracing methods
- **Radiocarbon content** can be used to identify biogenic content (**pure/blended**)
- Further **refinement** of radiocarbon method e.g. adjustment factors
- Identify the **impurity profile** of methanol from different pathways



We hope our materials are valuable to your work.
If they are, please consider citing us—proper attribution supports our efforts to keep developing high-quality resources for the community.

Thank You

Contact Us

@Maritime Energy & Sustainable Development Centre of Excellence (MESD)

D-MESD@ntu.edu.sg

https://www.ntu.edu.sg/mesd-coe

Scan to follow MESD on LinkedIn