

A NOVEL METHOD FOR GRAPHENE, GRAPHITE & HYDROGEN PRODUCTION

A new technology that directly converts petroleum feedstocks into products for clean energy storage and generation.

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The Global Challenge

Climate change, caused by global warming, is responsible for increasing ocean temperatures, melting of polar ice and glaciers that lead to rising sea levels, and an increased frequency of extreme weather events¹.

These issues threaten food production, lead to increased health issues and pose significant risks to economic growth. Those from low socio-economic backgrounds, both in developed and developing countries, are most vulnerable².

A key cause of global warming is the increased concentration of greenhouse gases in the Earth's atmosphere, largely because of burning fossil fuels as an energy source. Carbon dioxide is the greenhouse gas most cited for causing global warming³.

The development of energy sources that reduce or eliminate carbon dioxide emissions is critically important to mitigate against global warming. The Paris Agreement, a legally binding international treaty on climate change adopted by 196 parties at COP21 (Paris, 2015), aims to limit global warming and will require governments to reduce greenhouse gas emissions⁴.

¹ <https://www.gov.uk/guidance/climate-change-explained>

² IPCC, 2014: Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change

³ <https://www.epa.gov/ghgemissions/overview-greenhouse-gases>

⁴ https://unfccc.int/sites/default/files/english_paris_agreement.pdf

⁵ <https://firstgraphene.net/new-route-to-hydrogen-and-graphene-based-battery-materials-funded-by-uk-government/>

⁶ J. Carpenter et al.: Hydrodynamic cavitation, *Rev Chem Eng* 2016

⁷ *Science* (American Association for the Advancement of Science), 1990-03-23, Vol.247 (4949), p.1439-1445

⁸ *Petro Chem Indus Intern*, 2020 (<https://opastonline.com/wp-content/uploads/2020/01/various-ways-for-increasing-production-of-middle-distillate-pcii-20.pdf>)



Cavitation: A novel technology for process intensification

The single-step, scalable process is based on cavitation, which involves the formation, growth and collapse of vapour bubbles in a liquid due to rapid changes in pressure. This occurs over a very short timescale – typically fractions of a second. When the vapour bubbles collapse, they convert pressure into heat energy.

The intense energy that is released in the cavitation process can be applied to a range of processing technologies, such as waste-water treatment, biodiesel synthesis, water disinfection, the preparation of nano-emulsions and nanoparticle synthesis.

There are two methods for producing cavitation in liquid systems⁶:

- **Hydrodynamic cavitation** caused by pressure changes in a fluid as it passes through a constriction
- **Acoustic cavitation** from pressure variations due to sound waves passing through the fluid

In both cases, very localised regions of high temperatures (1000 – 10000 K) and pressures (100 – 1000 bar) are formed. This is equivalent to the temperature at the sun's surface and pressure in the deepest trenches of the ocean.

Due to the localised nature of the reaction, the bulk fluid remains at ambient pressures and temperatures.

First Graphene has exclusive access to this technology, which uses readily available processing equipment⁷.

A New Approach

First Graphene, in collaboration with Kainos Innovation Ltd and supported by the UK Government's Sustainable Innovation Fund⁵, has developed a novel technology based on a patented process that uses cavitation chemistry to convert petroleum feedstocks into high purity graphene, graphite and clean hydrogen.

These products play an important role in low carbon energy generation. High purity graphite and graphene are critical minerals used in batteries for energy storage, including those used in the electric vehicle market. Hydrogen is a clean fuel that does not produce carbon dioxide emissions when used as an energy source.

The government funding was used to prove the concept of the process, combining the scientific knowledge from Kainos Innovation with First Graphene's expertise in manufacturing operations, scale-up and commercial application development.

An Alternative Route for Petrochemical Processing

First Graphene has proven that the cavitation process can be used to process petroleum feedstocks that contain polycyclic aromatic hydrocarbons (PAHs) into graphene, graphite and hydrogen. These PAHs contain two or more aromatic rings and are present in middle distillate petrochemical fractions. There is a reducing demand for PAHs because of health and environmental concerns as well as economic factors⁶.

The chemistry takes place by a cyclodehydrogenation reaction:



A combination of *cata*- and *peri*-condensations results in the growth of 2-dimensional sheets, leading to the creation of graphene, as shown below in Figure 1.

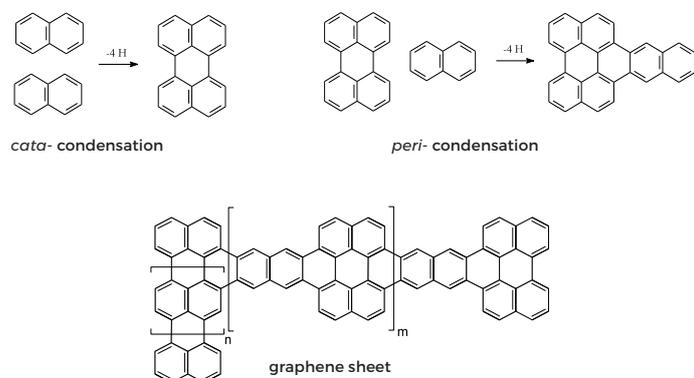


Figure 1. Reaction Mechanism

As the cavitation process progresses, clear liquid feedstocks change to a black colour (Figure 2), indicating the presence of graphene and graphite platelets in the product.

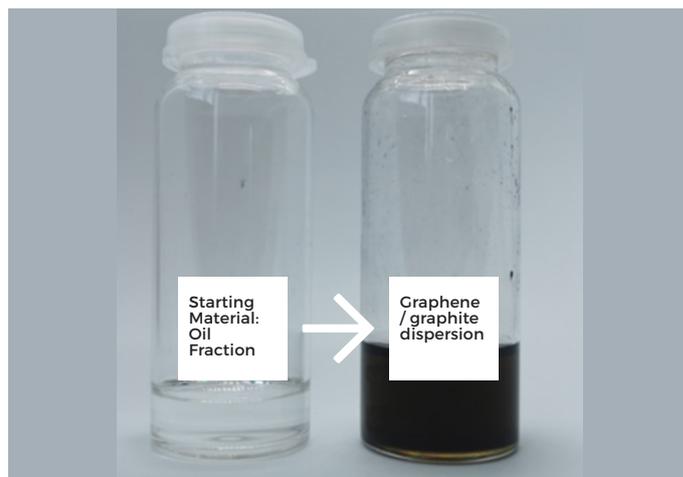


Figure 2: Conversion of feedstocks

A schematic of the process is shown below:

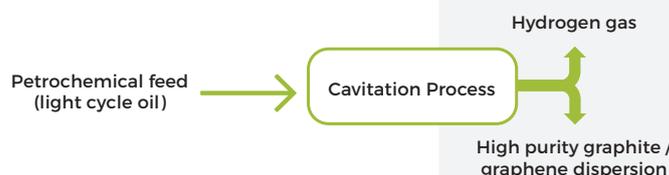


Figure 3. Process route

The cavitation process would most suitably be located within an existing oil refinery, where the full range of feedstocks and petroleum engineering capabilities are readily available. A direct feed will allow for a cost-effective capture of the created graphite and evolved hydrogen.

High Quality Products

The chemical reaction shown in Figure 1 is a "bottom-up" production route for synthesis of high purity graphene and graphite. The product quality has been confirmed by scientists at the company's state-of-the-art facility at the Graphene Engineering Innovation Centre in Manchester, UK. Analysis by techniques such as scanning electron microscopy (Figure 4) and Raman spectroscopy (Figure 5) confirms that pristine graphene and graphite is produced.

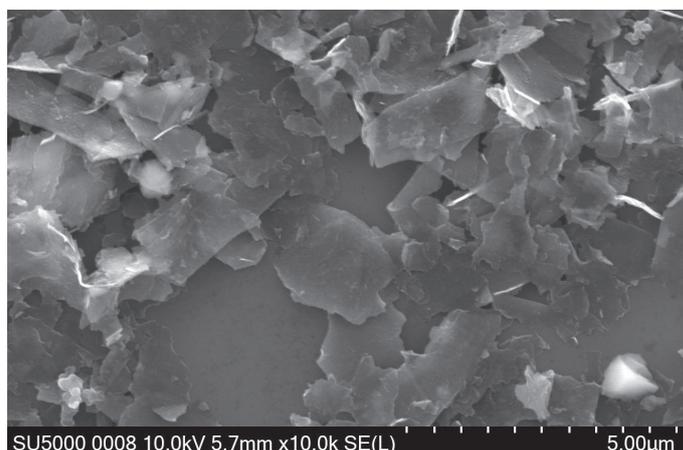


Figure 4. SEM Image of high-quality graphitic flakes from the process

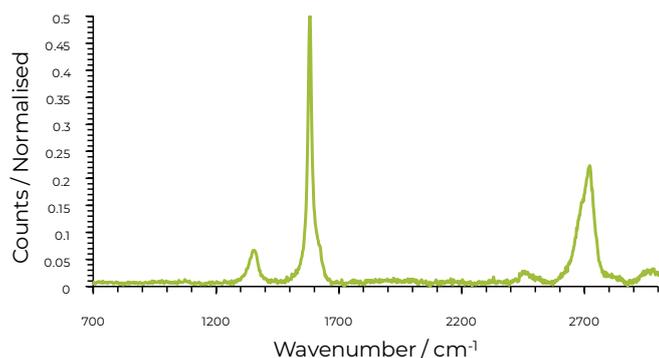


Figure 5. Raman Spectrum showing the high-quality graphitic flakes in the product

Given that the technology produces high purity graphitic materials with negligible metal contaminants, the materials are suitable for use in a range of high value applications, such as:

- Battery anodes or coated cathodes, which among other uses are applicable for electric vehicle batteries
- Graphite electrodes for electrode arc furnaces

Graphite for battery grade materials

High-purity graphite is required for batteries, for example in electric vehicles. Today, battery-grade graphite is made from:⁹

- **Natural graphite**, which involves an acid leaching step that is time consuming and can cause serious pollution, deterring its production in many parts of the world
- **Synthetic graphite** produced by high temperature treatment of petroleum by-products which is energy intensive and costly

As the demand for electric vehicles increases many companies around the world will need to source the raw materials required for battery production. The European Union has listed graphite as a critical raw material.

Hydrogen - A Valuable By-product

The hydrogen produced as a by-product can be used to generate clean energy. The advantage of using hydrogen as a fuel is that it does not generate harmful carbon emissions. Among other uses, this could be fed back into the refinery to reduce reliance on traditional energy sources.

The hydrogen generated in the cavitation process is genuine "green hydrogen", consuming less energy to create than "blue hydrogen" and generating no CO₂ by-products.

First Graphene estimates that from every tonne (1,000kg) of petroleum feedstock, 940kg of graphene/graphitic carbon and 60kg of green hydrogen gas can be produced.

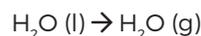
Routes to H₂ production: Thermodynamics

A brief comparison of the thermodynamics of hydrogen production is presented below:

Steam reforming of methane¹¹

An established process that uses high temperature steam (700 - 1000°C) to produce hydrogen from a methane source (eg natural gas) in the presence of a catalyst at a pressure of 3 - 25 bar. Carbon dioxide is produced as a by-product and must be sequestered.

The reaction scheme is:



This process is **endothermic**: $\Delta H_R^\circ +63 \text{ kJmol}^{-1} \text{ H}_2$

Pyrolysis of methane¹²

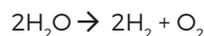
This process involves the splitting of methane into its elemental components - carbon and hydrogen. A range of process technologies, such as plasma reactors, molten metal reactors or conventional gas reactors can be used. Carbon black is produced as a potentially useful by product.



This process is **endothermic**: $\Delta H_R^\circ +37 \text{ kJmol}^{-1} \text{ H}_2$

Electrolysis of water¹³

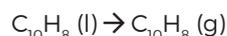
This is an electrochemical process which involves splitting water into hydrogen and oxygen using direct current electricity. Whilst this process does not directly produce carbon dioxide, it requires a renewable energy source to be considered a "green hydrogen" production technique.



This process is **very endothermic**: $\Delta H_R^\circ +286 \text{ kJmol}^{-1} \text{ H}_2$

Cavitation of diaromatics¹⁴

This process is the subject of this White Paper. It has the unique combination of being exothermic, does not produce carbon dioxide and produces a valuable, unique product in the form of graphene and graphite platelets.



This process is **exothermic**: $\Delta H_R^\circ -24 \text{ kJmol}^{-1} \text{ H}_2$ meaning, uniquely, energy is released in the process.

A comparison of the 3 alternative processes, with the Cavitation Chemistry Process as the baseline on the X-Axis, normalised to 0kJ / mol is shown in Figure 6 below.

The Cavitation Process is the most thermodynamically favourable, with other potential benefits including simplicity, unique by-products and potential to be integrated into existing petrochemical facilities.

⁹ International Journal of Mining Science and Technology 29 (2019) 671 - 689

¹⁰ <https://www.argusmedia.com/en/news/2144154-graphite-firms-integrate-european-battery-supply-chain>

¹¹ <https://www.energy.gov/eere/fuelcells/hydrogen-production-natural-gas-reforming>

¹² Energy Conversion and Management: X 7 (2020) 1000432

¹³ <https://www.energy.gov/eere/fuelcells/hydrogen-production-electrolysis>

¹⁴ Ultrasonics - Sonochemistry 56 (2019) 466-473

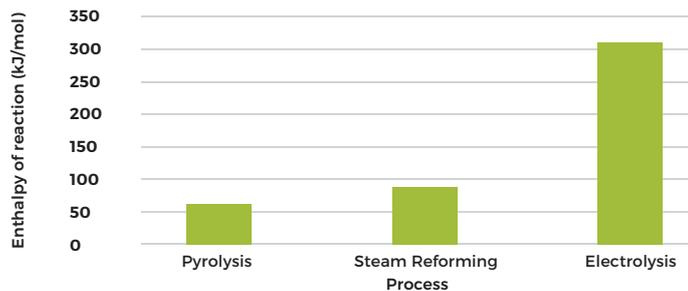


Figure 6. Reaction thermodynamics compared to Cavitation Process (Baseline)

Key Benefits

- The single step process **directly converts** petrochemical feedstocks into useful products - graphite, graphene and hydrogen gas
- Can be **upscaled** using readily available process equipment
- No carbon dioxide is produced
- The hydrogen gas has the potential to be used as an energy source within the chemical processing plant

Opportunities and Next Steps

First Graphene has proven the technology at the laboratory scale and is currently validating the quality and consistency of the resulting products.

The company is actively seeking **collaborative partners in the oil industry** that can work with the company to develop a pilot plant and prove the capability at scale (see Figure 7).

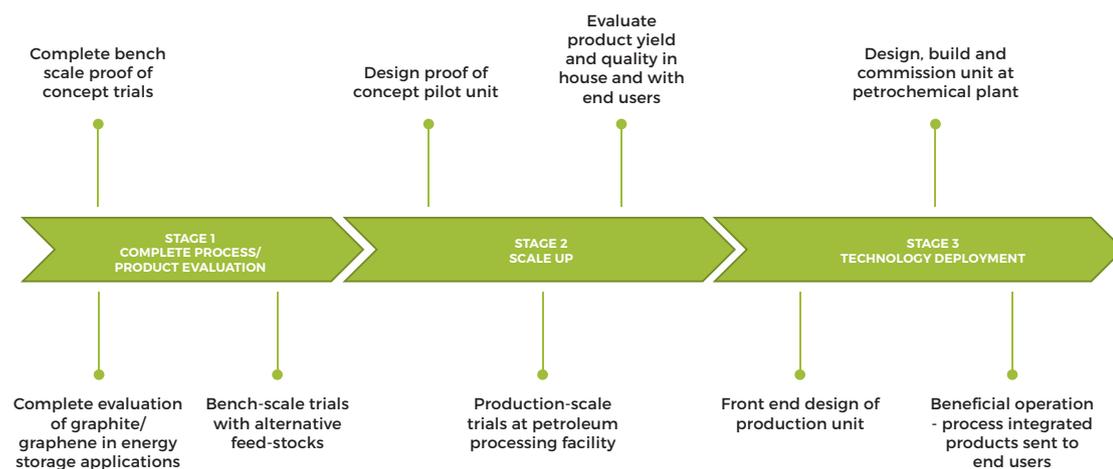


Figure 7. Development Roadmap

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