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Review

A Review on Recycling waste polyethylene materials into useful products via pyrolysis

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ABSTRACT:

From the viewpoint of reducing the environmental load and securing domestic resources in the future, it is essential to promote the recycling of waste plastics. The effective utilization rate of waste plastics in Japan has been increasing year by year, reaching 83 % in 2014. However, the percentages of material recycling and chemical recycling in the effective utilization rate are low at only 26 % and 4 %, respectively, and the remaining 70 % is only thermal recovery. In other words, there is a great potential for improving the effective utilization rate through material recycling and chemical recycling. In this paper, we focus on the thermal decomposition method of waste plastics, which is one of the chemical recycling methods. The thermal decomposition method makes it possible to convert mixed waste plastics, etc., into oil and gas, which are difficult to apply to material recycling. However, in reality, polyvinyl chloride (PVC) and polyethylene terephthalate (PET) generate corrosive gases and high-boiling point sublimable substances by thermal decomposition, which cause a decrease in the quality of the pyrolysis products and corrosion and clogging of the processing equipment, so waste plastics with a high resin content remain difficult to process. In order to overcome these problems, the authors have been studying the dry and wet dehydrochlorination and dechlorination processes for PVC, and the pyrolysis of PET to oil using lime. In this paper, we first summarize the current status of pyrolysis research on the major resins polyethylene (PE), polypropylene (PP), and polystyrene (PS), and then introduce the pyrolysis research on PVC and PET, focusing on the dehydrochlorination and dechlorination processes for PVC that the authors have reported, and the pyrolysis of PET to oil using lime.

KEYWORDS: Plastic pyrolysis, Waste management, Circular economy, Thermochemical conversion, Plastic-to-fuel, greenhouse gases, post-use plastic pyrolysis.

INTRODUCTION:

The recycling industry together with the waste management operators are facing two common challenges related to development of new business: most of easily recyclable waste is already being recycled and secondly, the secondary raw materials markets are challenging as prices of secondary raw materials compared to primary raw materials are not typically price competitive and overall the markets for secondary raw materials are still not properly established. Chemical recycling technologies [2,58,60] are likely to play a crucial role in the transition towards circular economy and closed-loop recycling of materials and compounds like hydrocarbons. These technologies enable the removal of hazardous substances and thus the handling of challenging waste streams. Commitment from materials and chemicals producers to use raw materials from secondary sources is a prerequisite for the development of sustainable, feasible and cost-efficient chemical recycling value chains[1] .

Pyrolysis processes are generally classified into low, medium and high temperatures based on the range of temperatures used to destroy the plastic structure. The corresponding temperatures defining the pyrolysis states are with the following temperature ranges less than or equal to 600°C, 600–800°C and greater than 800°C. The products obtained from pyrolysis of plastics depend on the type of plastics, feeding arrangement, residence time, temperatures employed, reactor type and condensation arrangement. Low temperature processes generally enhance liquid products and high temperature processes enhance gaseous products. Some polymers such as; polystyrene and poly(methyl methacrylate) undergo to produce monomers and other mono-aromatics besides other hydrocarbons. However, polyethylene and polypropylene having 0 and 2% monomer yield should not be used for monomer production processes. These kind of polymers undergo pyrolysis process to produce valuable hydrocarbon[2] . Plastics play a vital role in the human's daily lives because they are tactical in sectors like packaging, construction, motoring, electronics or agriculture and the others. So far, the use of plastic in modern life has become more widespread and unavoidable, resulting in an annual increase in global plastic production from various industries and households .Plastic waste fractions constitute a large portion of inorganic fractions of municipal solid waste (MSW), moreover, plastic waste accounts for roughly 10 % ∼ 13 % of the entire MSW throughout the world . Polyethylene (PE) and polypropylene (PP) are the most commonly used polymers in different applications among all the other types of plastic. The extreme use of plastic, the inappropriate management and disposal have resulted in negative influences on the environment and global ecosystem[3] .

In many nations including the United States, plastic waste disposal is a serious issue because it is difficult due to non-biodegradable nature of plastic . Moreover, it poses a significant environmental danger as it endangers the welfare of marine and terrestrial species and pollutes the atmosphere . After the initial usage, more than 60 % of the total plastic solid waste (PSW) generated is thrown in landfills around the world and less than 10 % of plastic waste is recycled . The discarded plastic that ends up in the ocean creates a massive plastic soup and garbage patch like the great Pacific garbage patch endangering the health of aquatic animals[4] .

The average plastic content of municipal solid waste in Western Europe is 9.1 wt%, representing more than 13 million tones of plastic waste generated in Western Europe each year (APME, 2004). However, the recycling rate for the plastic fraction of municipal solid waste remains below 10%, representing a waste of a resource (APME, 2004). The recycled plastic may be added to virgin plastic during the process. Applications for plastic mixtures have included plastic fencing, industrial plastic pallets, traffic cones, playground equipment and garden furniture. Other uses for recycled plastic products include their use in the construction industry for pipes, damp-proof membranes, plastic lumber and plastic/wood composites (Williams, 2005)[5] . The most common types of polyethylene are low density polyethylene (LDPE) and high density polyethylene (HDPE). They are produced as low or high density PE by addition polymerization of the ethylene using organometallic catalyzers. LDPE has a high degree of short- and long-chain branching, which means that the chains do not pack into the crystal structure as well. HDPE, which polymer chain may be 500,000 to 1,000,000 carbon units long with little branching, has a greater proportion of crystalline regions and therefore is harder and opaque than LDPE. HDPE has a large area of usage. 40% of produced HDPEs are used in production of many plastic belongings such as bottles for drink, food, cleaning products, etc. 30% of it are used in packaging, thin film coating, productions of pipe, tube and cable (Kurbanova et al., 1997)[6].

SECTION SNIPPETS:

Plastic waste resources:

Plastic waste resources are mainly divided into two categories: (1) pre-consumer or industrial plastic wastes and (2) post-consumer or municipal plastic wastes. The municipal plastic wastes primarily consist of polypropylene (PP), poly vinyl chloride (PVC), polystyrene (PS), poly ethylene terephthalate (PET), low-density polyethylene (LDPE) and high-density polyethylene (HDPE).

Pyrolysis is a good way to recycle energy from waste as it converts waste into high-energy liquid and gaseous materials . The pyrolysis of plastic waste takes place at temperatures ranging from 200 °C to 1300 °C depending upon pyrolysis methods and materials used.

the typical process involved in the pyrolysis of plastic waste. First, the plastic is uniformly heated to a limited temperature range with minimal temperature fluctuation and then oxygen is extracted from the[7]

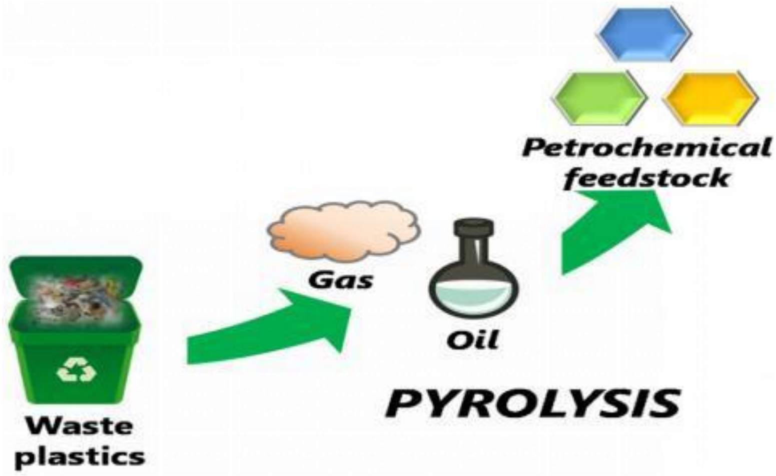

Figure : 1 converting waste plastic into raw materials and fuel through pyrolysis[7]. Products of plastic waste pyrolysis :

The pyrolysis process transforms plastic waste into organic vapors, gases, char, wax and HCl by thermal decomposition in the absence of oxygen. Thus, the primary product of the plastic waste pyrolysis process is liquid oil, while gases, wax, char, and HCl are by-products. Heating rate, temperature, pressure, type of reactor, catalyst and residence time are the main factors that can influence the percentage yields of pyrolysis products.

Pyrolysis of different plastics : Product output depends on the feedstock used, characterization of which can predict the product distribution to a certain extent. The proximate analysis measures the chemical properties of the feedstock according to four specific elements, including fixed carbon, moisture content, volatile matter, and ash content [18]. Based on previous research, high volatile matter (not less than 86.83 wt%) and low ash content (no more than 2 wt%) for: PET [19], high-density polyethylene (HDPE)[8].

Pyrolysis with different catalyst :

As described above, the thermal degradation of different plastics requires appreciable energy and elevated temperature to avoid wax and char formation. Another detriment exists, that a relatively broad spectrum of products, resulting from the thermal cracking of macromolecules to small molecules, complicates their current utilization on an industrial scale. Such obstacles will become even more disruptive when it comes to real-world plastic wastes in the commercial process[9].

Process optimization :

In catalytic pyrolysis systems, the key process parameters such as temperature, pressure, residence time, type and rate of fluidizing gas play important roles in the optimization of product yield and composition. The desired product can be obtained by controlling and adjusting the above parameters at different settings. In-depth discussions of these process optimization parameters are presented below.

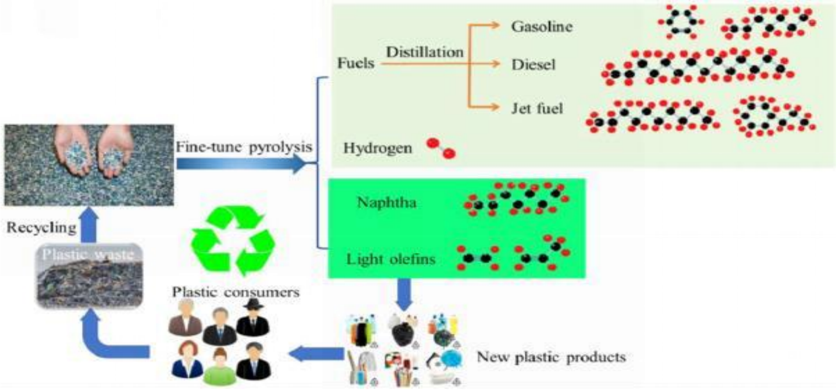

Figure 2 : pyrolysis technology for plastic waste recycling[9].

Product properties, upgrading and application :

Owing to the long hydrocarbon structure of plastic polymers and the different reactions taking place, catalytic pyrolysis technology usually converts plastic wastes into a mixture of products similar to the ones obtained by fractional distillation of crude oil, which range from refinery gasses, gasoline/naphtha, diesel to immobile residues. Since the liquid and gas fractions mainly consist of hydrocarbons and can be further converted into value-added fuels and monomers, this section will

Techno-economic assessment of catalytic pyrolysis systems :

Recycling of plastic wastes has developed into an urgent problem and society is approaching a key turning point. From an industrial level, several start-ups have been incentivized, and the governments are promising or taking action . Detailed case-specific techno-economic assessment is necessary to tell whether this growing industry can achieve feasible technologies with reasonable economic results, in which a sensitivity analysis is commonly performed to determine the most relevant

PSW pyrolysis for recovery of fuels or chemicals : Since mechanical recycling of PSW is hampered by high pre-sorting requirements and decreasing product quality in each cycle, chemical recycling can tackle these challenges and has attracted much interest from scientific and industrial communities. Research and development on chemical recycling of PSW, especially pyrolysis, seem to have made significant progress. The use of pyrolysis to recycle highly valuable products from PSW around the world shows a great potential.

Techno-economic analysis : The costs of PSW pyrolysis recycling, which will determine if it can be commercialized in the market, can be affected by many factors, such as labor, maintenance, transportation, capital investment, electricity, heat, and other plant utilities. The techno-economic evaluation of this process is essential to reduce the underlying costs of the process and improve the corresponding supply chain. This assessment and resulting recommendations will be beneficial to establish a sound strategic design[10].

Environmental considerations :

Life cycle assessment (LCA) plays an important role in identifying the environmental impacts of a product throughout its life cycle [247,248]. This tool can be used to compare different life cycles for alternative products and processes. As shown in four stages (the goal and define the system boundary, mass and energy flows, life cycle impact assessment for all processes, and sensitive analysis) need to be implemented. The final results obtained are beneficial to the product.

Quality of the feedstock :

Plastic waste is generally classified into two broad categories: post-industrial and postconsumer. The characteristics of these waste streams are quite different. While the postindustrial plastic waste is of clean, consistent quality and has usually defined composition, the plastic waste collected from consumers is rather dirty and is contaminated with different sorts of foreign materials including organic waste, wood pieces, glass, metals etc.

Feedstock availability :

The non-availability of plastic waste has been one of the main factors in the past why many plastic recycling initiatives failed despite being technically sufficient. In order to accomplish economically feasible pyrolysis of plastic waste, a steady flow of rather consistent quality feedstock is required. Also, pointed out by Ragaert et al , the economics is dependent on the large volumes of feedstock.

Feedstock preparation :

The HDPE and LDPE wastes were packages. These wastes were obtained from the separation and transfer station of a local solid waste collection company (in Konya-Turkey). Unwashed HDPE and LDPE wastes were shredded into approximately 8 mm pieces in lab-scale plastic crusher equipped with six blades and having bottom sieve of 8 mm pore size. HDPE and LDPE plastic wastes images, chemical formula and chain structures were shown in the carbon content of LDPE was higher than HDPE.

Steam cracking of pyrolysis oil and fossil-derived feedstocks : The estimations of the upstream life-cycle impacts and emissions of the steam cracking operation were based on the model by which is available in the Greenhouse Gases, Regulated Emissions and Energy Use in Technologies model . A portion of co-produced hydrogen and methane from the cracker is considered to serve as process fuels, reducing the use of external energy inputs. The modeling assumes that 70% of facilities in the United States use the co-produced hydrogen as an internal energy source while the remaining 30% is sold as an external product [11].

Pretreatment :

Cost-efficient pretreatment is needed however, the number of unit operations in pretreatment should be minimized to support economical feasibility. One example utilized and further developed in the WasteBusters project at VTT is a new type of modular extruder mixer (MODIX) , which is capable of processing organic waste and recycling material otherwise not suitable to be fed to pyrolysis, like fluffy plastic films, plastic bottles, canisters and mixed plastic waste including paper.

Opportunities related to the operational environment: Sustainability

Compared to the high number of life cycle assessment (LCA) studies focusing on waste incineration, pyrolysis of waste has not been given much attention. In the context of the WasteBusters project, the climate impacts related to pyrolysis of plastic waste were studied using the LCA methodology. LCA is a quantitative environmental impact assessment method, which can be used for evaluating the environmental impacts of products covering their whole life cycle.

Challenges related to the operational environment: Legislation

The legislative framework relevant for pyrolysis of plastic waste can be considered as complex, as it includes policies related to circular economy, waste management, product safety and fuels. For example, due to safety reasons, there are several requirements imposed by the legislation that prevent the use of recycled plastics in food contact materials and toys, which are among the most common uses for plastic. In case the end-product is used as a fuel, the GHG savings criteria set out.

Effect of the pyrolysis temperature on the product yields :

The yields of pyrolysis products are given in Table 3. For HDPE plastic wastes, gas production changed in the range of 9.12–10.34% at 300-600 °C pyrolysis temperatures. When temperature was increased to 700 °C, gas production reached 14%. As temperature increases, polymeric structure of the plastic is more degraded and new gas products are created. This is simply because of higher breakage in the structures of organic molecules with the effect of temperature. Gas product occurring at the end [12].

Purification stage :

After the conversion process, the pyrolysis oil was purified through hydrotreatment, to reduce the chlorine concentration from 600 ppm to 10 ppm . Energy requirements and type of energy sources were modeled from current refinery operations for crude oil, and hydrogen consumption was estimated from the stoichiometric amount required to convert the removed chlorine into hydrochloric acid. Although fluorine, diolefins, and silicon are other contaminants of concern, their removal in the hydrotreatment modeling was not considered due to insufficient information of the fluorine and diolefin concentrations and silicon removal technologies. Therefore, it was considered that focusing only on chlorine removal could provide a close approach to current operations. After purification, the pyrolysis oil is blended with feedstocks from refinery at the SR described before[13].

Life-cycle analysis

This study analyzed two perspectives: 1) steam crackers' perspective and 2) plastic recyclers' perspective. The first perspective analyzed the results when pyrolysis oil is co-fed with conventional feedstocks (gases and naphtha) at 5% and 20% SRs. The second perspective also analyzed the results from co-feeding but allocated the impacts associated with the substitution of conventional feedstocks with pyrolysis oil to a plastic with hypothetical 100% recycled feedstock. The results are reported using a functional unit of one kg of HDPE or LDPE, depending on the plastic under evaluation. A graphical description of these two perspectives is presented in figure[14].

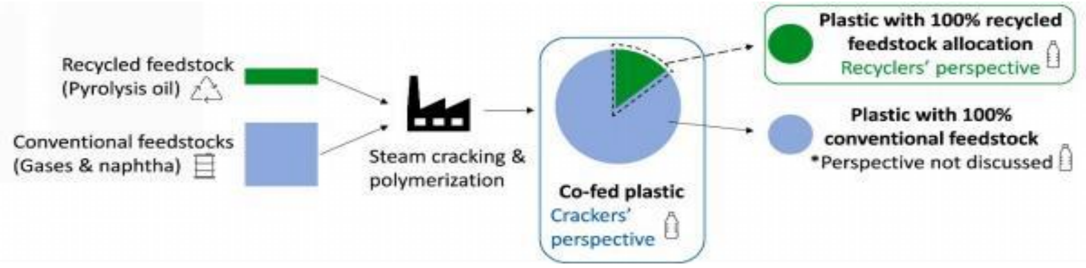

Figure : 3 life cycle analysis of recycling of post use plastic to plastic via pyrolysis[14].

Influence of Plastic Types :

The impact of catalyst on the composition of plastic oil is discussed later, in Section 3.1.2. The desired pyrolysis temperature to achieve a high conversion of polyolefins is above 450 ◦C, since, below this temperature, the solid residue drastically increases. Polystyrene (PS), which is composed of styrene monomers, can generate a liquid with a remarkable amount of aromatic compounds, such as benzene, toluene, and ethyl benzene . Although the pyrolysis of polyolefins and polystyrene leads to the formation of a liquid oil which can be an excellent precursor for fuels/chemicals, the pyrolysis of PET and PVC generates a significant amount of benzoic acid and hydrochloric acid, respectively, which are toxic and corrosive to the reactors[15]. Influence of Temperature :

Temperature plays a key role in all pyrolysis processes, regardless of the feedstock type. In the pyrolysis of plastic wastes, as in any other pyrolysis process, the increase in temperature results in a rapid increase in gas yields from the enhanced cracking reactions and, correspondingly, in a decrease of the oil/wax yield (Table 4). In addition to the alteration of yields, temperature expectedly affects the products quality, due to its impacts on the pyrolysis kinetic mechanisms. Generally speaking, high temperature favors the production of less waxy and more oily compounds production, attributed to the conversion of long-chain paraffins/olefins to shorter molecules. Conversely, the solid residue yield decreases at elevated temperatures. A qualitative assessment of plastic oil shows high temperature favors an increase in gasoline production corresponding to a higher concentration of aromatics . Flash Pyrolysis :

In order to avoid over-cracking reactions during pyrolysis, especially at high temperatures (above 700 ◦C), which converts a significant amount of liquid to gaseous products, flash pyrolysis taking place within milliseconds is a suitable option. Unlike the fast pyrolysis of biomass, which generates the highest yields of bio-oil, flash pyrolysis of plastic waste produces more gas rather than liquids (Table 5). As illustrated in Table 5, up to 75 wt.% of monomers, i.e., ethylene and propylene, can be recovered through flash pyrolysis. The byproduct, which is oil, can be used to provide the required energy for the process. Kannan et al. [56] performed a flash pyrolysis of LDPE in a microreactor with a minimal heat/mass transfer resistance at temperatures of 600– 1000 ◦C, and vapor residence time of 250 ms to investigate the effect of temperature on monomer recovery (yield of olefins). They found that the 950–1000 ◦C temperature range is optimal to recover up to 68 wt.% of monomers.

Hydrogenation : Hydrogenation process takes place in the presence of three components: hydrogen, a catalyst, and an unsaturated compound. The transfer of hydrogen pairs to the unsaturated compound is facilitated via a heterogeneous catalyst which enables the reaction to occur at a lower temperature and pressure. For instance, hydrogenation converts alkenes to alkanes in plastic oil [67]. Due to the significant presence of unsaturated compounds in the plastic oils, some storage instability challenges may be experienced over time[16].

Carbon Nanotubes :

Carbon nanotubes (CNTs) have gained recognition as very attractive materials due to their unique properties, including great electrical conductivity (100 times greater than copper), excellent mechanical strength (100 times greater than steel), high thermal conductivity, stable chemical properties, extremely high thermal stability, and an ideal one-dimensional (1D) structure with anisotropy . Conventionally, methane, natural gas, acetylene, and benzene from nonrenewable resources have been utilized as a feedstock for CNTs production. Recently, the potential fabrication of CNTs from the pyrolysis of plastic waste has drawn researchers' attentions, adding a significant value to the plastic wastes. The process of converting plastic waste into CNTs is composed of two successive stages (Figure 3). In the first stage, the plastic waste is converted to the volatile vapor in the absence of oxygen and at a moderate temperature (approximately 550 ◦C). Then, the produced vapor is introduced into the second stage at a high pressure of 1 MPa and a temperature of 750 ◦C in the presence of Ni-based catalyst where it is converted into CNTs on the surface of the catalyst through the chemical vapor deposition mechanism. In this advanced process, CNT yields can reach up to 25 wt.%[17].

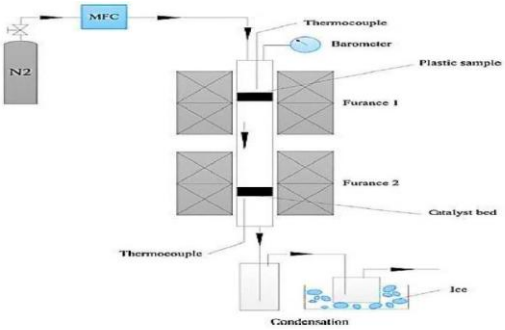

Figure : 4 Schematic diagram of two-stage pyrolysis reactor system[17].

Plastic Oil Cracking : utilized a two-stage unit, including a liquid–liquid extraction followed by a pyrolysis reactor, to investigate the thermal cracking of pyrolysis plastic oils containing considerable amounts of aromatic compounds, such as styrene. In the first stage, sulfolane solvent was used to remove the aromatic compounds prior to the pyrolytic cracking, in order to mitigate the coking effects, since stable aromatics (e.g., styrene) tend to be coked rather than cracked during pyrolysis. The results were promising, and the gas yield reached 85 wt.% at 750 °C, corresponding to a 20 wt.% increase compared to non-extracted oil. A schematic diagram of the pyrolysis oil cracking set-up is shown[18].

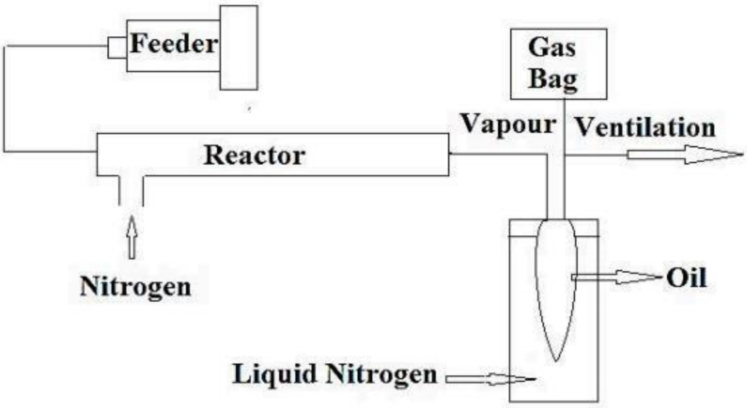

Figure :5 Schematic diagram of the experimental apparatus for cracking of raw plastic pyroland extracted oil after separation of aromatics[18].

CONCLUSION:

Accelerating the circular economy around plastic materials will be critical in decreasing the impact of plastic waste into the environment. Despite the great promise of plastic pyrolysis, several bottlenecks still limit its industrial scaling and worldwide adoption. Bottlenecks include the high energy input needed to achieve complete plastic conversion, the relatively poor understanding of kinetic reactions and corresponding mechanisms, and limited results in terms of real waste experiments. Scientists and engineers will need to address these bottlenecks soon. Nevertheless, the analysis and review of twenty years of published research suggests that thermochemical routes will continue being a focal point or “hot topic” in coming years.

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