Applied Mechanics and Materials Vol. 664 (2014) pp 80-86
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doi:10.4028/www.scientific.net/AMM.664.80

Submitted: 28.08.2014
Accepted: 28.08.2014

A Framework for Conversion of Plastic Waste into Fuels and Chemicals: A review of the waste current situation in Libya

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Keywords: Plastic waste; recycling of polymers; waste management.

Abstract. Pyrolysis of waste plastics is one of the routes used for waste minimization, which has been gaining interest in recent years as a feedstock method.
In this work, the two universal problems: plastics waste and fuel shortage have been addressed simultaneously. The process of converting PP and PE plastics waste in Libya into fuel and chemicals was overviewed. Data concerning Plastic Industry in Libya was collected to which some projection of the future production rate and waste rate has been estimated.

Introduction

Plastic is the general common term for a wide range of synthetic or semi synthetic organic amorphous solid materials suitable for manufacturing of industrial products [1]. Plastics are typically polymers of high molecular weight, and may contain other substances in order to improve their properties. Plastics have several characteristics such as relatively low cost and the ease of manufacturing. So, plastic are extremely used in different products such as car parts, doll parts, soft drink bottles, and refrigerators …etc [1].
According to international statistical records, 260 million tons of plastic are produced in the world per year with an annual rise rate at approximately 5%, while 60% of all PSW goes to landfill [2]. As a result plastics waste management has become an essential issue world widely.
Three scenarios were adopted for the plastic waste management viz.: land filling, incineration and recycling [3] However, disposing of the waste to landfill is becoming undesirable due to legislation pressures (waste to landfill must be reduced by 35% over the period from 1995 to 2020), rising costs and the poor biodegradability of commonly used polymers.
There are four approaches that have been proposed for recycling of waste polymers [4, 5]: primary recycling, mechanical recycling, chemical recycling and energy recovery.
The most attractive method according to the principles of sustainable development is the chemical recycling method, which is also called as a feedstock or tertiary recycling.
The process of converting PP and PE plastics waste in Libya into fuel and chemicals was overviewed. Data concerning Plastic Industry in Libya was collected to which some projection of the future production rate and waste rate has been estimated.

Recycling of Plastic

A. *Definition of plastic*

Plastic is the general common term for a wide range of synthetic or semi synthetic organic amorphous solid materials suitable for manufacturing of industrial products [1]. Plastics are typically polymers of high molecular weight, and may contain other substances in order to improve their properties. Plastics have the unique capability to be manufactured in a way to meet specific functional needs of products. Plastic versatility allows it to be extremely used in industry, where it can be used in car parts, doll parts, soft drink bottles, and refrigerators …etc. [1].

Plastics have become an integral part of human lives. This is because plastics are relatively low cost and easily available for much more diverse applications[1]. Each year more than 100 million tones of plastics are produced worldwide [1].

The increased consumption of plastic materials was driven by the following Benefits [3]:

1. Extreme versatility and ability to be tailored in order to especially meet specific technical needs.
2. Lighter weight than other competing materials, which results in reducing fuel consumption during transportation.
3. Extreme durability.
4. Resistance to chemicals, water and impact.
5. Good safety and hygiene properties for food packaging.
6. Excellent thermal and electrical insulation properties.
7. Relatively inexpensive to produce.

B. Recycling of plastic approaches

The intensive use of plastic has led to a revolution in production and uses of plastics, which accumulates as Plastic Solid Waste (PSW) in the waste stream. According to international statistical records, 260 million tons of plastic are produced in the world per year with an annual rise rate at approximately 5%, while 60% of all PSW goes to landfill [2].

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There are four approaches that have been proposed for recycling of waste polymers [4,5]. The first approach is *Primary recycling, which is* referring to the "in-plant" recycling of the scrap material of controlled history. The second one is *Mechanical recycling*, where the polymer is separated from its associated contaminants and it is reprocessed by melt extrusion. The third one is *Chemical recycling which is* leading in total depolymerization to the monomers, or partial degradation to other secondary valuable materials. The last one is *Energy recovery*, which is an effective way to reduce the volume of organic materials by incineration.

Among the recycling techniques, incineration meets with strong societal opposition and mechanical recycling can be carried out only on single-polymer waste streams. However, the most attractive method according to the principles of sustainable development is the *chemical recycling method*, which is also called as a feedstock or tertiary recycling. According to this method, waste polymers can be either converted to original monomers or other valuable chemicals. These products are useful as feedstock for variety of downstream industrial processes or as transportation fuel.

The basis for such interest is energy content of these polymeric materials compared to domestic fuels and energy resources as shown below in Table 1 [6][*]:

Table 1: Plastic materials Latent Energy compared to traditional energy products

Polymers [MJ/kg]		Fuels [MJ/kg]		Biomass [MJ/kg]	
PE	-46.3	Coal	-32.5	Glucose	-15.55
PP	-46.4	Crude Oil	-46.3	Wood	-18
PET	-23.5	Biodiesel	-42.2		
PVC	-18	Natural Gas	-53.6		
PS	-41.4	Methane	-55.6		
		Hydrogen Gas	-143		
		Gasoline	-46.4		

*reproduced from raw data available in UNEP Compendium [6]

Polyolefin (LDPE, HDPE, PP) is a major type of thermoplastic used throughout the world in different applications such as bags, toys, containers, pipes (LDPE), house wares, industrial wrappings and film, gas pipes (HDPE), , battery cases, automotive parts, and electrical components (PP). In Western Europe alone approximately 41.37 million tones of these three polymers are consumed each year according to 2003 figures, which is representing a 56% of the whole consumed thermoplastics [7].
Addition polymers such as polyethylene, in contrast to condensation polymers; i.e. poly (ethylene terephthalate) (PET), cannot be easily recycled by simple chemical methods [8]. Instead, thermochemical recycling techniques like pyrolysis have been proposed. In this process is a series of refined petrochemical products are produced, particularly a liquid fraction similar to that of commercial gasoline [4].
Thermal cracking of polyethylene and polypropylene is usually carried out either in high temperatures (>700 ◦C), to produce an olefin mixture (C_1–C_4) and aromatic compounds (mainly benzene, toluene and xylene) or in low temperature (400–500 ◦C) (thermolysis) where three fractions are received: a high-calorific value gas, condensable hydrocarbon oil and waxes [9, 10]. In the first case, the objective is to maximize the gas fraction and to receive the olefins, which could be used after separation as monomers for the reproduction of the corresponding polyolefins [11]. Cracking in lower temperatures leaves as a waxy product from the reactor, which is mainly consists of paraffin together with a carbonized char.

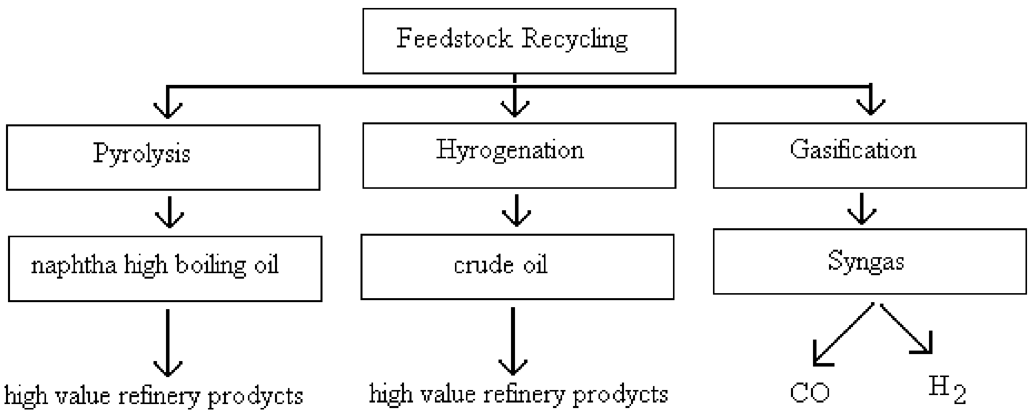

Fig.1 Plastics Feedstock Recycling Scenarios

The gaseous fraction can be used for the supply of the energy required for the pyrolysis after burning. The liquid fraction mainly consists of linear olefins and paraffin with C_{11}–C_{14} carbon atoms and it has only traces of aromatic compounds [8]. Thermal cracking of polyolefin proceeds through a random scission mechanism in four steps: initiation, depropagation, inter- or intra-molecular hydrogen

transfer followed by b-scission and termination. In general, thermal cracking is more difficult in HDPE followed by LDPE and finally by PP [12].
In the present investigation, the recycling of model and waste products are based on LDPE, HDPE and PP it to be examined using two different methods: the traditional method of dissolution/ reprecipitation and the more challenging technique of pyrolysis.
The first one belongs to the mechanical recycling techniques while the second one belongs to the chemical/feedstock recycling.
Weight percent amounts and temperatures using either model polymers as raw material or commercial waste products (packaging film, bags, pipes, food-retail products). This technique has been widely used by Papaspyrides et al.[13, 14, 15] and other researchers [16].
In this work, the process of converting plastics waste (Polyethylene, PE and Polypropylene, PP) into fuel and chemicals has been overviewed to prove such solutions are amicable for recycling of plastics in Libya. Experimental and design work for catalytic pyrolysis is expected to be carried out in a laboratory fixed bed reactor using as raw materials either a LDPE model, a HDPE model and a PP model or waste products based on these polymers. All gaseous and oil fractions' compounds from pyrolysis will be identified. Encouraging conclusions concerning alternative techniques of waste polymer recycling are expected.
Pyrolysis, also termed thermolysis is a process of chemical and thermal decomposition, generally leading to smaller molecules. In most pyrolysis processes, however, air is excluded, for reasons of safety, product quality, and yield. Pyrolysis can be conducted at various variables temperature levels, reaction times, pressures, and in the presence or absence of reactive gases or liquids, and of catalysts. Plastics pyrolysis proceeds at low temperature (<400°C), medium temperature (400–600°C) or high temperature (>600°C). Some preparation of the waste plastics feed is required before pyrolysis, including size reduction and removal of most non plastics.
It is thus quite obvious that a pyrolysis process for plastic waste yet need to be converted for more specific targets based on specific inputs and for specific material types.

Current situation in Libya

Table 2 shows the total polymers production capacities in Libya according to 2008 estimation. The total production of polymers is 384,000 tones/year. However, only 125,000 tones/year are consumed locally, which represents about 32.5% of the total capacity. On the other hand, 100,000 tones/year of plastic materials are imported, as shown in table 3.

Table 2: Total Polymers Production Local Capacities 2008 [17]*

Producer	Products	Production capacity [t/y]
Abu Kammash	ethylene dichloride (EDC)	104,000
	VCM	60,000
	PVC	60,000
Ras Lanuf Oil and Gas Processing Company	HDPE	80,000
	LLDPE	80,000
Total capacity		384000
Total consumption		125,000 (32.5%)

*reproduced from the reference [17]

Table 3: Imported Plastic materials specially PP and PE 2008 [17]*

Imported Items	tons	%
All plastic materials	100,000	-
Polyethylene	10,128	10.1%
Polypropylene	18,649	18.7%

*reproduced from the reference [17]

According to Table 4, the quantities consumed based on 2010 up to 2020 have been projected based on a 6% gross rate increment per year [17] and waste 10% per year [18] as shown in table 5. Table 6 shows the consumption based on Main Products

Table. 4: Consumption of polymers for local Libyan Industry 2010

	HDPE	LDPE	PVC	PP	PET	PU	Others PS, ABS
Consumption [tones]	23,940	5,580	29,700	8,850	64,00	15,000	1,000
Estimated Total [tones]	40,000	8,000	32,000	12,000	10,000	20,000	3,000
Percentage [%]	32%	6.4%	25.6%	9.6%	8%	16%	2.4%
Total [tones]	125,000						

Table 5: Projection of the PP and PE consumption and waste quantities up to 2020

Year	Polyethylene, PE [tons]	Polypropylene, PP [tons]	Total [tons]	Waste [tons]
2010	49,000	12,000	61,000	6,100
2011	51,940	12,720	64,660	6,466
2012	54,880	13,440	68,320	6,832
2013	57,820	14,160	71,980	7,198
2014	60,760	14,880	75,640	7,564
2015	63,700	15,600	79,300	7,930
2016	66,640	16,320	82,960	8,296
2017	69,580	17,040	86,620	8,662
2018	72,520	17,760	90,280	9,028
2019	75,460	18,480	93,940	9,394
2020	78,400	19,200	97,600	9,760
Total	700,700	171,600	739,020	73,902

Discussion

As shown in table 5, it is obvious that in 10 years time there will be an accumulation of PP and PE waste in such amounts 6,700 per year in average. This quantity unless being removed from the waste stream it will seriously impact the environment, especially if the ideal production capacities are considered, the sum of 160,000 tons per year will be available for the local market which will increase the consumption dramatically and hence the waste as well.

As being highlighted by UNEP [6], heating value is an important characteristic of solid fuels. Some examples of heating values of several types of waste and solid fuel are listed in Table 7.

Table 6 Consumption based on Main Products

No.	Products	Consumption [tons]
1	PVC pipes	24,000
2	PE blown film for shopping bags HD+LD	18,000
3	PE house ware	15,000
4	PET bottles	10,000
5	PET water tanks	4,000
6	HIPS thermoforming	2,000
7	PVC window profiles	3,000
8	PVC cables	5,000
9	UP foams	15,000
10	PE blown film for agriculture	2,000
11	Injection products, agriculture, building etc	5,000
12	Others	12,000
	total	125,000

Table 7 Heating values of various fuels and waste

Fuel or waste	Typical heating value [kcal/kg]
RDF refuse derived fuel	4,000-5,000
RPF refuse-derived paper and plastic fuel	6,000-8,000
coal	6,000-8,000
Heavy oil	9,500
Wood/paper	4,300
Plastics (polyethylene)	11,000
Typical municipal wastes	1,000-1,500

It is quite obvious according to table 7 that the heating values of Polyolefins(PP and PE) is considerably higher even than the traditional fuel and energy products, thus encourage researchers to proceed to convert these materials into solid and liquid fuels.
Since the average yield percentage is about 80%, the 6,700 tons of waste per year could restore at least 5,360 tons of fuel, which will secure a valuable amount of energy per year.

Conclusion and Recommendations

The two universal problems: plastics waste and fuel shortage have been highlighted in this work. The importance of converting PP and PE plastics waste in Libya into fuel and chemicals was overviewed. Data concerning Plastic Industry in Libya was collected to which some projection of the future production rate and waste rate has been estimated.
The quantities of LDPE, HDPE and PP in Libya for the next coming 10 years have been estimated, which will increase waste to 6,700 ton per year. This amount has to be recycled in order to avoid impacting the environment.
The best way as previously proposed is to recycle these waste into useful products such as fuel or/and chemicals by designing appropriate waste management scenario. By doing so a considerable amount of fuel could be restored. At least 5,360 tons of fuel per year could be restored from this amount of 6,700 tones per year.

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