



Combustible Gases from Low Density Polyethylene via Low Temperature Catalytic Pyrolysis

Nguamo S.*, Ijuo G. A., Oloruntoba S.O.

Department of Chemistry; Federal University of Agriculture, PMB, 2373, Makurdi, Nigeria

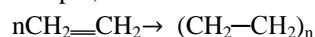
*Corresponding author's email address: surmanguamo@gmail.com

Abstract A cylindrical pressure cooking pot of height 30 cm with an internal diameter of 31.5cm was adapted for the pyrolysis of low density polyethylene (LDPE) in the presence of Fluid Catalytic Cracking (FCC) catalyst. The gases evolved were collected and analysed using Tedlar bag and a BUCK 530 Gas Chromatograph respectively. At 150 °C and 250 °C and at catalyst/sample ratio of 1:8, the pyrolysis reaction using fresh FCC catalyst showed aliphatic hydrocarbon in the range of C₁ – C₉ corresponding to the total concentrations of 82.4914 and 192.2153 respectively. The values (ppm) obtained at 150 °C and 250 °C using catalyst/sample ratio of 1:16 to be 92.2837 and 485.8220. With spent FCC catalyst at 150 °C and 250 °C using catalyst/sample ratio of 1:8, the total concentrations (ppm) obtained was 92.4257 and 116.9178, while the corresponding values (ppm) at catalyst/sample ratio of 1:16 was 65.3531 and 120.1380 respectively. Aliphatic hydrocarbons (C₁ – C₉) were the main fuel gases revealed which can be fractionated into gasoline range gases and organic solvents.

Keywords Pyrolysis, Low density polyethylene (LPDE), FCC catalyst, aliphatic hydrocarbon

Introduction

Plastic is a high molecular weight material which has its commercial history traced to about 1869 when John Wesley seeking for a substitute to ivory developed a practical process for converting cellulose nitrate into useful products. Plastics are referred to as polymers, the term polymer means a molecule made of repetition of a simple unit. All plastics are large molecules made up of long chains of atoms covalently bonded together [1]. The structure of polyethylene for example, can be written in a form as shown below.



Polyethylene



Plastics which are also known as polymers are among the most commonly used materials in daily life and with that comes an environmental concern regarding the disposal of their waste. The same chemical bonds are responsible for both the durability and resistant to natural processes of degradation of plastics [2]. Based on its chemical structure, synthesis process, density and other properties, they can be classified in many ways. In order to assist recycling of the waste plastic, society of plastic industry (SPI) defined a resin identification code system that divides plastic into

the following seven groups based on chemical structure and application. PET, HDPE, PVC, LDPE, PP, PS, Other [3]. The above seven plastic products as follows:

One of the major concerns for the extensive use of plastics is the disposal of waste plastic material after use. Developing countries like Nigeria are faced with municipal and public waste management problem, which has constituted the greatest environmental problem. As a result of the present economic situation, low-density (LDPE) sachet serves as the cheapest packaging material in Nigeria. It has become popular in almost all the communities but unfortunately this has led to new source of enormous solid waste owing to the fact that LDPE degrades very slowly. The cities are therefore, stinking from this heavy unmanageable solid waste [4]. The cheapest method for conversion of the LDPE waste to useful products is through pyrolysis [5]. The process of pyrolysis involves the heating of the sample in the absence of oxygen so that the organic compounds are decomposed, generating gaseous and liquid products which can be used as fuels/or sources of chemicals. The part of the sample which is inorganic, but free from organic matter remains unchanged in the solid fraction enabling their separation and recovery for reuse [6].

The resultant low quality products from thermal pyrolysis requiring high temperature has made this process unfeasible. The addition of catalyst which will lower the temperature and reaction time improves the thermal pyrolysis and allow the production of hydrocarbons with a higher added value, such as fuel oils and petrochemical feed stocks. This makes the use of pyrolysis an attractive technique for recycling waste plastics. The use of catalyst in pyrolysis process gives added value to the cracking efficiency which promotes the breaking of C-C bonds and also determines the length of the products obtained [7-9]. This work focuses on low temperature catalytic pyrolysis of post-consumer LDPE waste with the effect of FCC catalyst in other to recover fuel gases from them.

2. Experimental

2.1 Materials: LDPE sample collection and preparation

From refuse dumping sites around Makurdi town, Benue State of Nigeria was collected the low density polyethylene waste (LDPE). After thorough washing using detergent and rinsed properly with deionized water, the samples were dried at room temperature to remove all moisture. This was closely followed by reducing the dried samples into smaller bits to increase the surface area [10]. The Fluid Cracking (FCC) catalytic used was obtained from Nigerian National Cooperation (NNPC) Warri in Delta State. Analysis showed the catalyst to be composed of aluminum and silicon. From the SEM images, it was deduced that the catalyst particle size ranged within $5\mu\text{m}$ - $80\mu\text{m}$ while the spent FCC catalyst gave particle sizes within the range of $8\mu\text{m}$ - $100\mu\text{m}$. The composition of the fresh and spent FCC catalyst (ppm), by the help of Atomic Absorption Spectrometry (AAS) analysis was found to be 5.122 and 3.375 of aluminum while silicon was found to be 6.480 and 5.270.

2.2 Experimental Procedure

A Presto pressure cooking pot made of stainless steel of height 30.00 cm with an internal diameter of 31.50 cm was converted to a fixed bed reactor and adapted for the pyrolysis reaction [11].

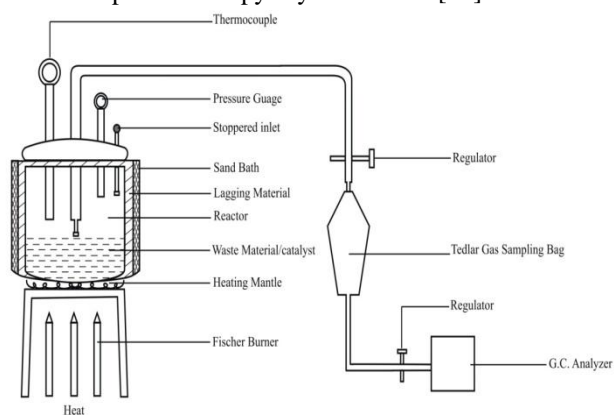


Figure 1: Layout of the pyrolysis process



The evolved gases were collected from an outlet tube which was placed at the top of the cover. The lagged reactor with a fire blanket was placed in sand bath constructed with iron sheets for heat retention. This was heated with three Mekker burners in order to attain the required temperatures and were controlled by means of a thermocouple as shown in *Figure 1*. The gases evolved were collected with the aid of tedlar bags. These gases were immediately sent for gas chromatogram for analyses.

2.3 Catalytic Cracking of LDPE

Two catalyst/sample ratios (1:8 and 1:16) were investigated in the catalyzed pyrolysis as described in [12]. 200 g of the polymer material sample was placed at the bottom with the catalyst material arranged in sandwich layers within the polymer and evolution of gases started slightly evident by the swelling of the bag. After heating for about $1\frac{1}{2}$ hours at 250 °C, the system was shut down. The gases collected at these different temperatures (150 °C and 250 °C), labeled in the tedlar bags were analyzed. The system was shut down allowed to cool before the reactor was opened. The residue for each run was weighed.

3. Results and Discussion

3.1 Results of Gas Chromatographic Analyses obtained from the reaction between the sample and fresh FCC catalyst

As shown in *Figure 2*, the composition of gases obtained from catalytic pyrolysis of waste water sachets (LDPE) at 150 °C and 250 °C using fresh FCC catalyst with catalyst/sample ratio of 1:8. The total concentration of gases obtained at 150 °C was analysed to be (82.4914) while that obtained at 250 °C was (192.2153). The gases produced were within the carbon member range of C₁ - C₄ and C₆ - C₉ for both reactions occurring at 150 °C and 250 °C.

It is therefore observed that the total concentration of gaseous products increased with increase in temperature [13-14]. The carbon atoms obtained at both temperatures are aliphatic in nature which is in accordance with the expectation that the bi-modal pore size distribution and mild properties of FCCs would allow the formation of more paraffin, this agrees with results presented by Lee and Shin [15]. It was observed that the total concentration of gaseous products obtained in the pyrolysis reaction was lower using FCC catalyst than that obtained when the zeolite catalyst was used on HDPE and PET with the reactions occurring under the same conditions. This is in agreement with the literature that zeolite favour the production of gaseous products in fuel feed stock recycling [16-17]. This high gas yields in zeolite catalyst reactions can be employed by the fact that the micro porous structure of zeolite have a higher internal surface than the external surface and thus enables hydrogen transfer between these surfaces [18]. However, it was generally observed that the FCC catalyst in pyrolysis reactions will result in more gasoline range products and this evident from the result.

The dominant components obtained from the gas chromatographic analysis of the results at 150 °C were observed in C₂ (17.7218 ppm), and C₃ (10.6437 ppm), C₇ (15.0540 ppm), C₈ (16.4300 ppm), and C₉ (13.3415 ppm). The dominant components obtained from the results of gas chromatographic analysis at 250 °C were C₂ (40.4245 ppm) C₃ (34.3444). The results of gas chromatographic analysis at 250 °C were C₂ (40.4245 ppm) C₃ (34.3444 ppm), C₇ (27.5187 ppm), C₈ (39.5082 ppm), and C₉ (35.0203 ppm).

Similarly, results obtained from pyrolysis of LDPE at 150 °C and 250 °C using catalyst/sample ratio of 1:16 as presented in *Figure 3* gave the total concentrations of gases at 150 °C and 250 °C to be (96.2830 ppm) and (485.8220 ppm) respectively. The gaseous products increased with increase in temperature, indicative of the fact that the effect of the catalyst on the yields and structure of products becomes less significant with increasing temperature, [19-20].

From the results of the gases collected at catalyst/sample ratio of 1:16, the dominant components were C₂ (24.0675 ppm), C₃ (13.0870 ppm), C₆ (18.4109 ppm), C₇ (16.4109 ppm), C₈ (16.7121 ppm) for the gases collected at 150 °C. The result of the gaseous components collected at 250 °C reveals that the dominant components were C₂ (147.8199 ppm), C₃ (26.3320 ppm), C₄ (27.7833 ppm), C₇ (67.8705 ppm), C₈ (116.9201 ppm) and C₉ (91.7324 ppm).

One of the dominant components observed in C₂ can be explained with the structure and degradation pattern of polyethylene [21].



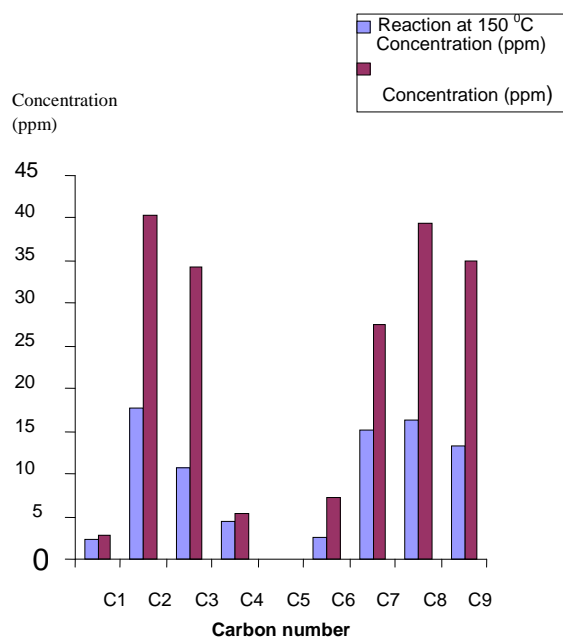


Figure 2: Composition of gases obtained from Catalytic pyrolysis of waste LDPE at 150 °C and 250 °C using fresh FCC catalyst at catalyst/sample ratio of 1:8

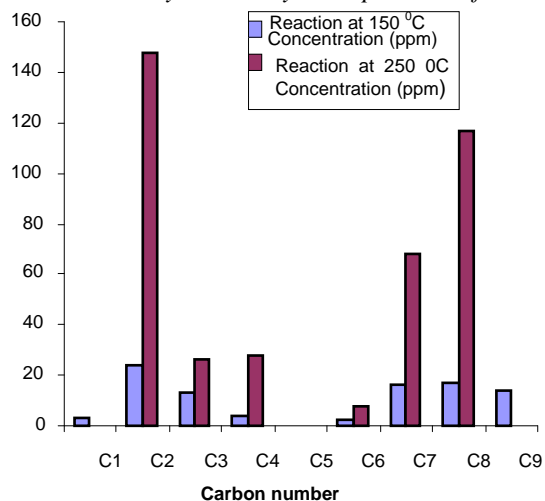


Figure 3: Composition of gases obtained from Catalytic pyrolysis of waste LDPE at 150 °C and 250 °C using fresh FCC catalyst at catalyst/sample ratio of 1:16

3.2 Results of Analyses of gases obtained from Catalytic Pyrolysis of the Samples using Spent FCC Catalyst

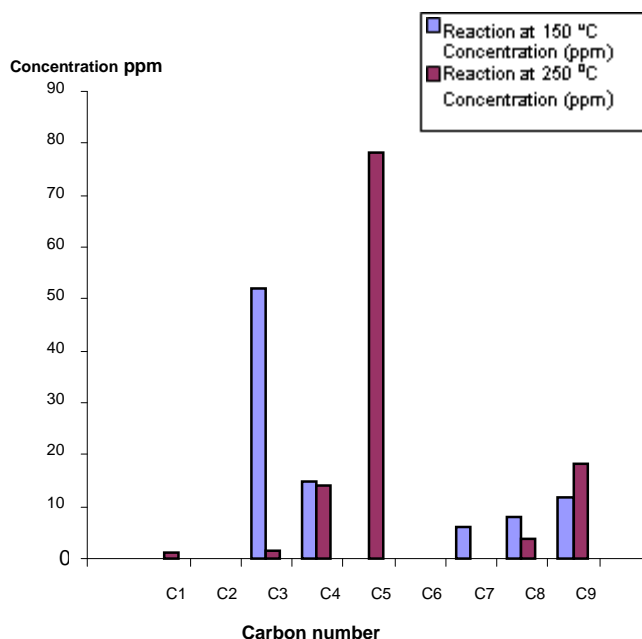


Figure 4: Composition of gases obtained from Catalytic pyrolysis of waste LDPE at 150 °C and 250 °C using spent FCC catalyst at catalyst/sample ratio of 1:8

Figure 4 show the composition of gases obtained from catalytic pyrolysis of waste water sachets (LDPE) at 150 °C and 250 °C using spent FCC catalyst with catalyst/sample ratio of 1:8. The analysis of the result show that the total concentration of gases obtained at 150 °C yielded (92.4257 ppm) while that at 250 °C gave a total concentration of (116.9178 ppm). The gases produced were within the carbon number C₁ – C₉ for the reactions at 150 °C and 250 °C. It is therefore observed that the total concentration of gaseous products increased with increase in temperature. The carbon atoms obtained from the analysis of the gases collected at both temperatures are aliphatic in nature which is in agreement with the expectation that the bi-modal pore size distribution and mild properties of FCCs would allow the formation of more paraffin.

It is also observed that the total concentration of gaseous products obtained with pyrolysis reaction of LDPE using spent FCC catalyst is lower than that obtained with fresh FCC catalyst. This is in accordance with the expectation that the spent FCC catalyst would exhibit slightly lower activity, but despite their diminished activity, these catalysts were still significantly effective compared to the results obtained by pure thermal cracking of LDPE.

The dominant components obtained from the gas chromatographic analysis of the result obtained at 150 °C were observed in C₃ (52.2025 ppm), C₄ (14.7871 ppm), C₇ (5.9285 ppm), C₈ (7.8664 ppm) and C₉ (11.6339 ppm). On the other hand, the dominant components obtained results of gas chromatographic analysis at 250 °C were C₄ (18.2544 ppm), C₅ (78.0995 ppm), and C₉ (18.2544 ppm). The dominant carbon atoms obtained at both temperatures of 150 °C and 250 °C were within the range of C₃ – C₉. This result is in agreement with results presented by Cardona and his co-workers [22], when they compared the selectivity of various silica-alumina and Y-zeolites with spent FCC catalyst over PP and found a comparable gasoline range yield in the spent FCC catalyst (greater than 70 %).

The result of gas chromatographic analysis of gases obtained from pyrolysis of LDPE at 150 °C and 250 °C using catalyst/sample ratio of 1:16 as presented in Figure 5 gave a total concentration of gases at 150 °C and 250 °C to be (65.8876 ppm) and (120.1308 ppm) respectively. It is observed that the gaseous products increased with increase in temperature. This shows that the effect of catalyst yields on the structure of the products becomes less important with increasing temperature. Coke formation is a common problem with the FCC catalyst in pyrolysis research as



the activity of the catalyst is expected to drop with increasing coke content [22], but here, higher gaseous content were achieved at a longer time as the gases collected at 250 °C were more in concentration.

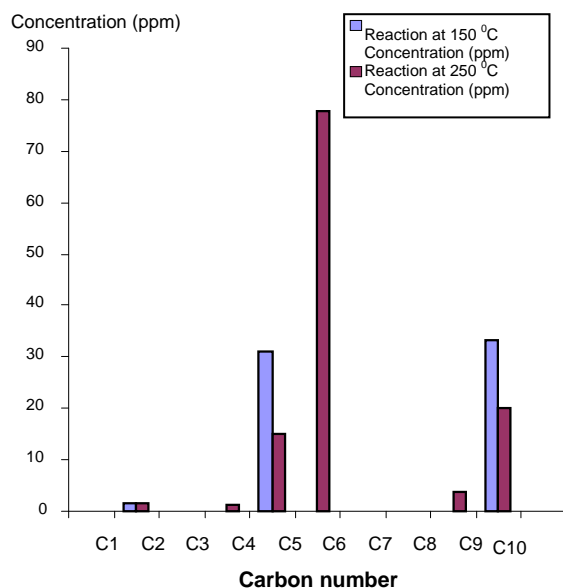


Figure 5: Composition of gases obtained from Catalytic pyrolysis of waste LDPE at 150 °C and 250 °C using spent FCC catalyst at catalyst/sample ratio of 1:16

4. Conclusion

In this work, Combustible Gases from Low Density Polyethylene via Low Temperature Catalytic Pyrolysis was studied using fresh and spent FCC catalyst. It was observed that the pyrolysis reaction using fresh FCC catalyst gave aliphatic hydrocarbon within the range of C₁-C₉ for the reactions which occurred at 150 °C-250 °C using catalyst/sample ratio of 1:8 and 1:16 respectively. The corresponding values of aliphatic hydrocarbons within the range of C₁-C₉ were obtained for reactions using spent FCC catalyst for the reactions which took place at 150 °C-250 °C using catalyst/sample ratio of 1:8 and 1:16 respectively. It was observed from these results that both fresh and spent FCC catalyst resulted in the formation of fuel gases as reasonable amounts of C₁-C₄ gases were obtained. Reactions involving both fresh and spent FCC catalyst also gave gasoline range products as reasonable values were obtained within the range of C₇-C₉. The catalytic pyrolysis of HDPE using FCC catalyst (fresh and spent) has not only reduced the solid waste by 50% and 62.5% as well as 50% and 60% by volume for the reactions which occurred using catalyst/sample ratio of 1:8 and 1:16 respectively, useful gases which can be fractionated into fuel gases and gasoline range gases were also obtained.

Acknowledgement

The authors appreciate the assistance of the Head, Department of Chemistry and the technologist of the Mechanical Engineering Department, all of University of Agriculture, Makurdi, Nigeria, for access into the Lab and the construction of the cylindrical pressure cooking pot respectively.

Conflict of Interest

The authors declare no conflict of interest.



References

- [1]. Kent J. A., Reigel's Hand book in Chemistry 9th Edition. CBS publishers and Distributors, Darya Ganj, New Delhi-110 2(1997) 622.
- [2]. Schiers and Kanmisky, Feedstock Recycling and Pyrolysis of Waste plastics, Converting Waste Plastics into Diesel and other fuels. John Wiley and Sons Limited. (2006) 1-5.
- [3]. Stanitski C.L, Eubanks L. P, Middlecamp C.H., Stratron W.J., Chemistry in Context 3rd Edition. McGraw-Hill Higher Education. (2000) Pp341-350.
- [4]. Ademiluyi T, and Adebayo T. A. (2007). Fuel Gases from Pyrolysis of Polyethylene sachets. *Journal of Applied Science and Environmental Management* 11: 21-26
- [5]. Lopez A., De Macro I., Caballero B.M., Adrados A., and Lanesgoiti M.F. (2011). Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic waste. *Waste Management* (New York, N.Y), 31:1852-1858 <http://dx.doi.org/10.1016/j.wasman.2011.04.004>. pm. d:21530000221.
- [6]. Ceolho A., Costa L., Marques M.M., Fonseca I.M., Lemos M. A, (2012). The Effect of ZSM-5 Zeolite activity on the Catalytic degradation of High-density polyethylene using Simultaneous DST/TG analysis. *Applied Catalysis A: General* 413-414(2012)183-191 <http://dx.doi.org/10.1016/j.apcata.2011.11.010>.
- [7]. Panda A.K., Singh R.K, and Mishra D.K. (2010). Thermolysis of waste Plastics to liquid fuel. A suitable method for Plastic waste and Manufacture of value added products: A world perspective. *Renewable and sustainable Energy Reviews*. 14:233-248.
- [8]. Aguado J., Serrano D.P., San Miguel G., Escola J.M., and Rodriguez J. M. (2007). Catalytic Activity of Zeolitic and Meso-structured Catalyst in the Cracking of Pure and waste polyolefins. *Journal of Applied and Pyrolysis*. 78: 153-161 <http://dx.doi.org/10.1016/j.jaap.2006.06.004>
- [9]. Abdulkareem S.A, Eleburuikie N.A., and Amoloye T.O, (2014). Comparison of Fuel oil from Thermal Cracking and Catalytic of high density polyethylene. *Journal of Chemical Society of Nigeria*, 39: 103-106
- [10]. Smith J.M, Chemical Engineering Kinetics 2nd Edition McGraw Hill Kogakushha Ltd, (1993) 5-30
- [11]. Osueke C.O., and Ofondu I.O., (2011). Conversion of Waste Plastic Polyethleneto fuel by means of Pyrolysis. *International Journal of Advanced Engineering Sciences Technologies*, 4:2230-7818 <http://www.ijast.iserp.org.ISSN>:
- [12]. Demibras A. and Ahyam J. (2004). Pyrolysis of Municipal Plastic Waste for Recovery of Gasoline range Hydrocarbons, *Journal of Analytical and Applied Pyrolysis*, 72:92-102.
- [13]. Lee K. H, Shin D.H., and Seo Y.H. (2004). Liquid-phase Catalytic Degradation of mixtures of Waste High-density polyethylene and Polystyrene over spent FCC catalyst. Effect of mixing proportions of reactions. *Polymer Degradation and Stability*, 84:123-127
- [14]. Lee K.H, and Shin D.H (2003). Catalytic Degradation of waste HDPE over acidic catalyst with different pore sizes. *Journal of Industrial and Engineering Chemistry*, 9:584-589.
- [15]. Surma N., TorP.N., Ijuo, G.A. (2018). Useful Gases from Waste polyethylene Terephthalate via low temperature catalytic pyrolysis, *Chemistry Research Journal*. 3:57-63.
- [16]. Nwadinigwe C.A., Surma N., Alumona T.A., Ezeofor C.C., and Lawal A.M. (2018). Urban mining of Fuel gases via Low Temperature Pyrolysis of Post-consumer High Density Polyethylene Waste, *J. Appl. Sci. Environ. Manage*, 22: 945-948
- [17]. Nwadinigwe C. A. (2012). Basic Principles of Organic Chemistry: WIPRO International, 101
- [18]. Zeng G.M., (2003). Performance of Liquid Fuel Catalytic Cracking of waste plastics in a Fluidized bed. *Energy Sources* 26: 557-569.
- [19]. Murata K., Sato K., Sakata Y., (2004). Effect of Pressure on Republic, Thermal Degradation of Polyethylene. *Polymer Degradation and Stability*, 72:519.



- [20]. Borsidi N., Miskolczi N., Angyal A., Bartha L.L., Kohan J., and Lengyel A., (2001). Hydrocarbons obtained by Pyrolysis of Contaminated Waste Plastics. 4th International Petroleum Conference. Bratislava, Slovak, (2011) 1-9
- [21]. Cardona S.C., and Corma A. (2000). Tertiary Recycling of Propylene by Catalytic cracking in a Semi batch stirred reactor- Use of Equilibrium FCC commercial catalyst. *Applied Catalysis B-Environmental*, 25:151-162.
- [22]. Ofoma I. (1006). Catalytic Pyrolysis of Polyolefins. A thesis presented to the Academic Faculty, Georgia Institute of Technology in partial fulfillment of the requirements for the degree of Masters in Science, (2006) 1-29.

