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A Review Paper on Utilisation of used PPE Kits in a Sustainable Way

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Abstract: This paper provides an updated review on conversion of used PPE kits into useful biofuels by pyrolysis and catalytic pyrolysis i.e., converting the polypropylene (PP) plastic (which is a major constituent of PPE kits) into biofuels -which is also a standard fossil fuel .This study suggests a strategy that could help to alleviate the problem of dumped PPE, which is currently being disposed of at unprecedented scale due to current situation of COVID-19 pandemic and is going to be a potential threat to the environment. In this way, we will not only reduce the accumulated waste, associated risks to the humankind and environment but we can also produce a useful source of energy.

Another way to convert PP into oil is by using supercritical water at 380-500°C and 23MPa over a reaction time of 0.5-6 hrs.
Keywords: Pyrolysis, Catalytic pyrolysis, Polypropylene (PP), ZSM-5, Supercritical water.

I. INTRODUCTION

A. Preface

In India, the very first case of coronavirus was reported on 30th January ,2020 but within a very short period of time, it spread all over the country [1]. To combat covid-19, India adopted some strategies as per the WHO guidelines. As positive cases of coronavirus increased day by day, the need for the PPE kits were also increasing, this means the problem arising from disposing of PPE kits were also increasing, which will become a threat to our future. According to WHO, till 8th April 2020, 22,073 health workers in 56 countries have been infected by covid-19. Till now, coronavirus has been spread to over 192 countries. The total covid-19 positive cases are 11, 07, 20, 226 and 24, 51, 739 have died. Among these, 4, 59, 30, 720 are active cases and 6, 23, 37, 767 have been recovered as of 20th February,2021. In India, there are 1, 09, 77, 387 covid-19 positive cases. Out of which, 1,56,240 have died. The number of active cases is 1, 43, 099 and 1, 06, 78, 048 have been recovered as on 20th February, 2020 [2].

B. About PPE kits

The PPE kits are widely used for protecting the wearer from various hazards like: physical injury or contagious infections, it is often termed as ‘protective clothing’. There are different types depending on their usage like respirators, eye protectors, for armed forces, skin protection, head protection, etc. The PPE kits are now used in heavy amounts amid pandemic i.e., COVID-19 [3]. There are various reports emerging which cite the littering due to onetime use masks, since masks are a major used protective equipment which is also advised by WHO to be worn when in public. Masks are worn by almost all people whereas the whole PPE kits can only be used by doctors or for extensive use, which can clearly justify the reason for mass dumping of masks. The most used PPE kit in 2020 amid COVID-19 includes head cover, goggles, face shield, mask, gloves, gown/aprons, shoe covers. Each component having its own significance in protection from any contagious viruses/infections. The face shields and goggles are generally made with highly transparent material so that it wouldn't hamper the visibility of the wearer. PP poses such a characteristic of being highly transparent [4]. PPE kits are not reusable and shared as its first acronym says it’s personal. So, the world is concerned about the problem of shortage as well as disposal of these PPEs at the higher level. However, CPCB has given the guidelines to deal with the biomedical and coronavirus -related waste but dumping at such a higher level is a major threat to the environment [5]

C. Components of PPE and it’s major raw materials / constituents:

The components of PPE are given below: [4],[6]

1) Gown
2) Gloves
3) Protective glasses / goggles
4) Face shield
5) Particulate respirator

6) Masks (N95/N99/FFP1/FFP2/FFP3)
7) Shoe covers
8) Head covers

Raw Materials, used in the Manufacturing of the Components of PPE are Shown in the Below Mentioned Table: I

Components of PPE	*Raw materials for their manufacturing*
Gown	Polypropylene, polyethylene, polyester
Gloves	PVC, rubber, latex, nitrile, neoprene
Protective Glasses	Polycarbonate, cellulose propionate
Face shield	Polycarbonate propionate, acetate, PVC, PTEG
Particulate respirator	Polypropylene
Masks (N95 and others)	Nonwoven Polypropylene
Shoe covers	Polypropylene, plastic, polyethylene
Head covers	Polypropylene, plastic, polyethylene

D. Polypropylene and some of its properties

It is a thermoplastic polymer, which is prepared by propylene catalytically. It's a semi crystalline resin. It has a wide range of applications in the world because of its excellent physical, chemical, thermal, and mechanical properties.

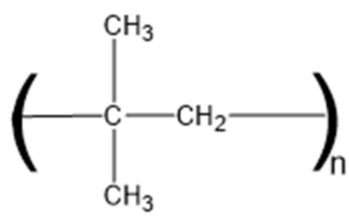

Figure.1: Structure of Polypropylene

1) Low density (1.04- 1.06 g/cm^3)
2) High melting temperature
3) Chemical inertness
4) Flame retardant
5) Excellent resistant
6) Flexible
7) High tensile strength
8) Semi rigid
9) Translucent

E. Types of PP and Configurations in which PP Exists

There are two major types of PP

Homopolymer and Copolymer as Mentioned in the Table: II

HOMOPOLYMER	*COPOLYMER*
Formed via addition polymerisation	Formed via condensation polymerisation
Contains single type of polymer	Contains more than one type of polymer
Melting point – 160-165^{0}C	Melting point – 135-159^{0}C
Good processability	High processability
Good impact resistance	High impact resistance
Main applications include textiles, healthcare, electrical, packaging, etc.	Main applications include pipes, housewares, construction products, automobiles, films, etc.

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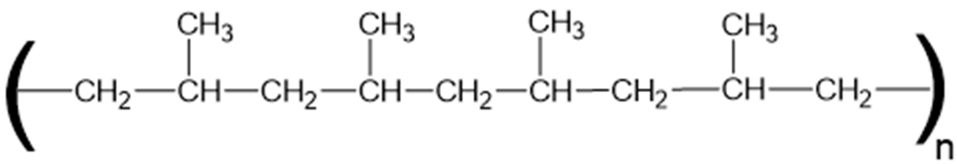
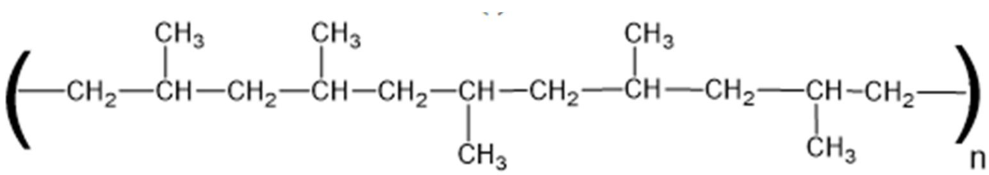
Table: III: Mechanical and Thermal Properties of PP

Property	Homopolymer			Copolymer	
Tensile strength (MPa)	34	30	29	29	25
Brittleness temp (°C)	+15	0	0	-15	-20
Impact strength (ft lb)	10	25	34	34	42.5
Melt flow index	3	0.7	0.2	3	0.2
Elongation at break (%)	350	115	175	40	240
Flexural modulus (MPa)	1310	1170	1100	1290	1030
Vicat softening point (^{0}C)	154-150	148	148	148	147
Rockwell hardness (R-scale)	95	90	90	95	88.5

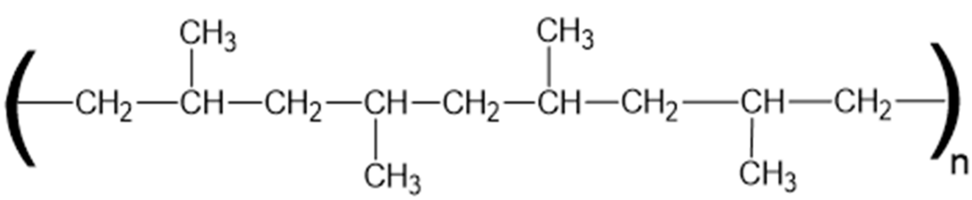
Polypropylene exists in three stereospecific configurations [8]:
1) *Isotactic:* When all the methyl groups are on the same side of the backbone of the polymeric chain.
2) *Atactic:* When the methyl groups are randomly attached to the backbone of the polymeric chain.
3) *Syndiotactic:* When the methyl groups are joined alternatively opposite to the backbone of the polymeric chain.



(a)



(b)



(c)

Figure.2: Configurations of Polypropylene (a) Isotactic (b) Atactic (c) Syndiotactic

Every plastic has a Resin identification code/plastic recycling code, which depends upon the type of resin used. PP's resin identification code is 5. Although PP is very popular among packaging goods in the world, still only 1% of PP is recycled, which means most of the PP is being dumped off or incinerated. Incineration of PP produces dioxins and vinyl chloride.

Some disadvantages of PP are summarised below: [7],[15]
a) It is degraded by ultraviolet (UV).
b) It is attacked by chlorinated solvents and aromatic solvents.
c) Burning of PP can discharge dioxins and vinyl chloride.
d) PP products degrade very slowly in the landfill. It takes approximately 20-30 years to decompose. This exhibits severe environmental concerns.

e) PP sometimes also contains some toxic additive metals such as lead and cadmium which react with organics to produce toxic leachate which is a potential source of groundwater pollution.

Apart from PPE, polypropylene is also used in various other things like packaging, plastic parts for industries like automotive, textiles, in making toys, hinges, crates, bottles, straws. All these can be converted into biofuel.

II. PYROLYSIS

A. Introduction

It is the method in which thermal decomposition of polymers takes place at a very high temperature and high pressure in the absence of oxygen. As its name suggests pyro (a Latin word) means “fire” and lysis (a Greek word) means “separation” or “splitting”. It is the most generally used method to convert or recycle plastic solid waste into useful biofuels. There is no need to separate a particular type of plastic during thermal pyrolysis. Basically, it involves the degradation or we can say, De polymerization of large polymers into smaller ones [9].

There are various catalysts, which are being used in pyrolysis to enhance the product selectivity and yield some of them are ZnO, MgO, $CaCO_3$, CaC_2, SiO_2, SiO_2-Al_2O_3, ZSM-5 (chemical formula $Na_nAl_nSi_{96-n}O_{192}\cdot16H_2O$; 0<n<27) zeolite, kaolin [10]. The fuel obtained is in liquid, solid and gaseous state. Thermal cracking or pyrolysis is done by free radical mechanism. There are three major steps in the mechanism which are given below:

1) Initiation
2) Propagation
3) Termination

B. Pyrolysis using catalyst Ahoko kaolin [11]

Pyrolysis is done by decomposing PP thermally, which is done in the absence of air and in presence of some inert gases like: nitrogen, argon [10]. The pyrolysis done at ~400 is slow mode of pyrolysis which will require quite a time to complete and the yield in liquid state is also quite low (~30%), pyrolysis done at ~500 is intermediate mode of pyrolysis which take average time to complete and the yield in liquid state is also fair enough(~50%) and lastly the pyrolysis done at >500 is the fast mode of pyrolysis which take a very short amount of time to complete and yield of liquid product is comparable to that of the intermediate pyrolysis [10]. Studies have shown that the thermal pyrolysis done ~450 yields the optimum results for pyrolysis of PP. In a particular study by researchers the polypropylene was subjected to pyrolysis by thermal degradation via CVD (chemical vapour deposition) in presence of nitrogen gas at a temperature of ~450 with a residence time of 30 min. and the percent yield obtained in different states are shown below in the pie chart [13].

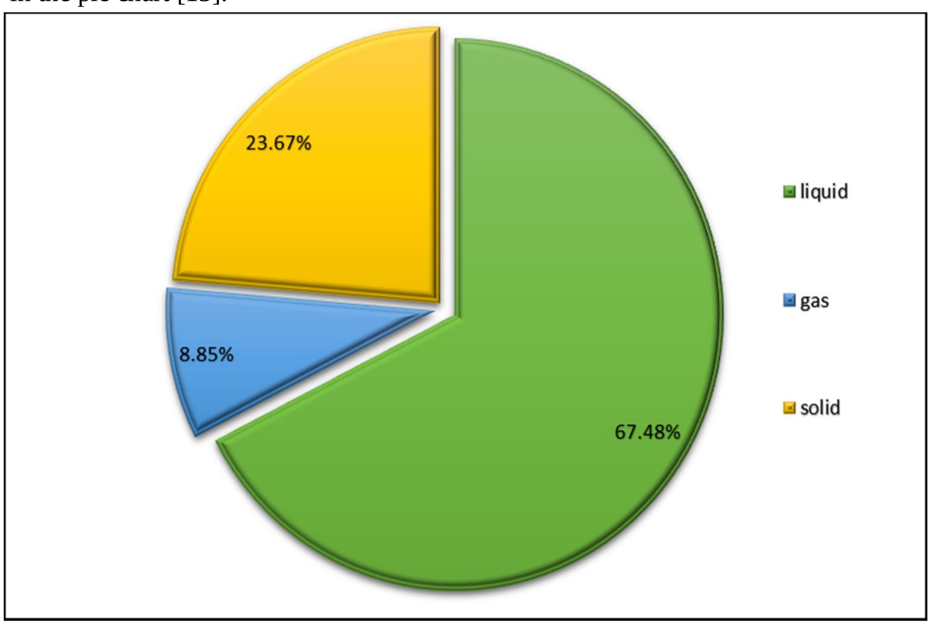


Figure.3: Thermal Pyrolysis Without Catalyst

Researchers then carried out the same thermal pyrolysis at ~450 via CVD in presence of nitrogen gas with the kaolin catalyst. They conducted this experiment in various ratios of catalyst: polypropylene starting with 1:1 till 1:20 but the effect of catalyst was only pronounced till the ratio 1:4 and after that effect was almost negligible on the yield obtained. The yields obtained in the different states of 1:1, 1;2, 1:3 and 1:4 ratios are shown below in the pie chart [12]. The highest yield of liquid which is most useful as a biofuel is obtained in the ratio 1:3.SO, we concluded that the ratio 1:3 is the most useful ratio.

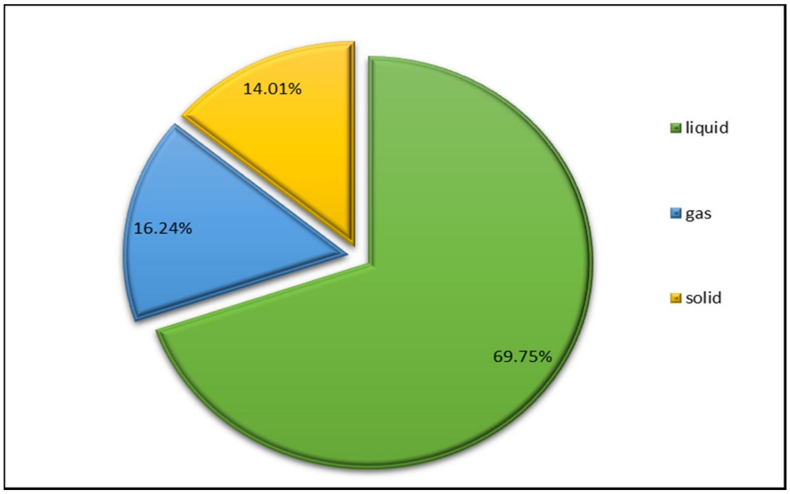


Figure.4: Catalytic Pyrolysis for 1:1 ratio (Catalyst: Polypropylene)

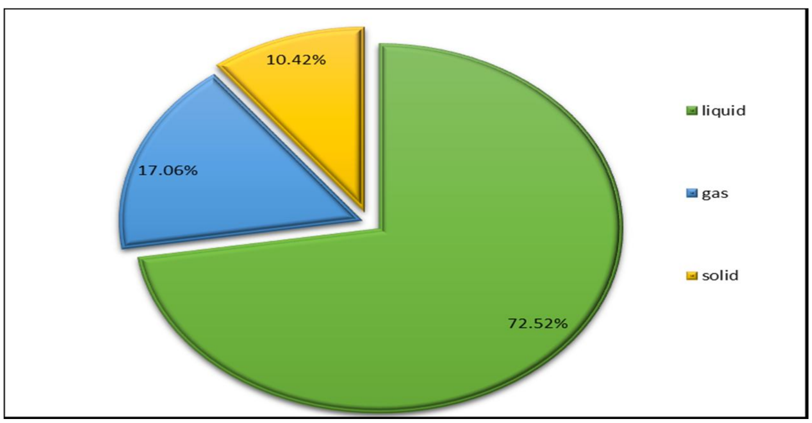


Figure.4: Catalytic Pyrolysis for 1:2 ratio (Catalyst: Polypropylene)

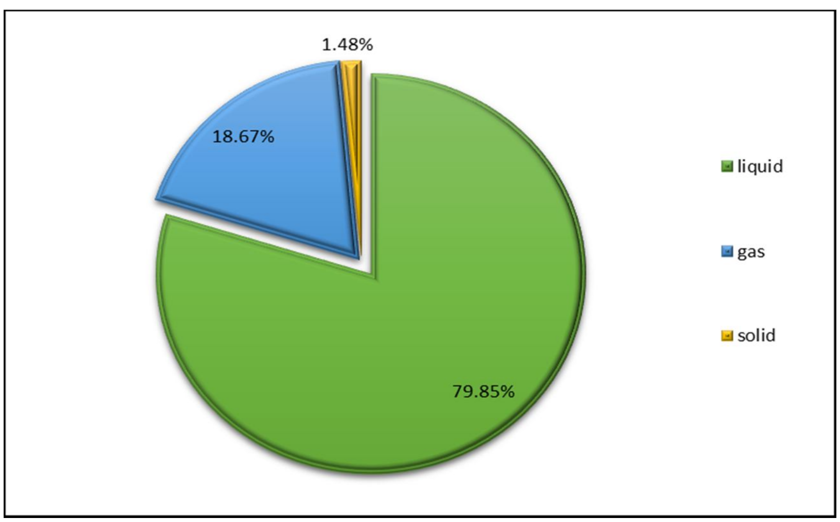


Figure.5: Catalytic Pyrolysis for 1:3 ratio (Catalyst: Polypropylene)

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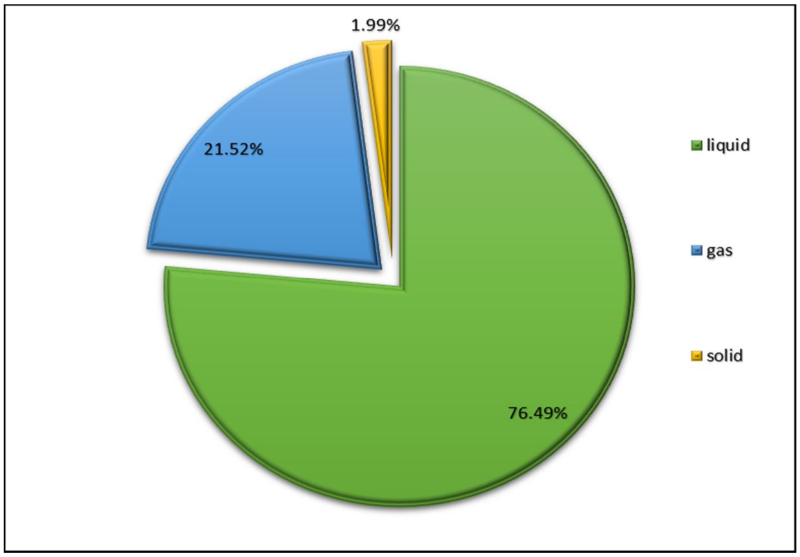

Figure.6: Catalytic Pyrolysis for 1:4 ratio (Catalyst: Polypropylene)

The catalyst used here is kaolin clay, which is very cheap as compared to other catalysts, making this reaction economical at large scale. These are found in abundance in the regions like India, Nigeria etc. The major component of kaolin clay is alumina i.e., Al_2O_3 and silica i.e., SiO_2 as these two are the basis of any type of clay. The other constituents include P_2O_5, K_2O, CaO, Sc_2O_3, TiO_2, V_2O_5, Cr_2O_3, Fe_2O_3, NiO, CuO, ZnO, Ga_2O_3, Rh_2O_3, Re_2O_7, Br [11]. Their composition depends on different factors like origin of clay, whether the clay is modified or not, etc.

C. Pyrolysis using ZSM-5 and Red Mud

Researchers have studied the effect of ZSM-5 and red mud in pyrolysis of PP. Red mud needs higher temperature for its catalytic effect in pyrolysis than the ZSM-5zeolite. The results of both the catalysts have been compared with the one without catalyst. It has been found that ZSM-5 zeolite has a stronger effect in the characteristics and distribution of pyrolysis products and also favours the production of lighter and more aromatic liquids [14].

D. Conversion of Polypropylene into oil by Liquefaction using Supercritical Water

The process of converting polymers into oil by using supercritical water is known as supercritical water liquefaction [https://www.sciencedirect.com/science/article/abs/pii/S0360544206000946]. The polypropylene polymer was fed on an autoclave with the supercritical water which undergoes the 3-stage process, in the 1st stage gaseous product was separated out then to the remaining reaction mixture DCM was added and in the 2nd stage the reaction mixture was filtered and the solid remains were separated out, the resulting mixture was then subjected to liquid-liquid separation from which aqueous and oily layer was separated [16]. The oil product was obtained as a mixture with DCM. This reaction was done at different temperatures with different reaction time and the percentage of product yields shows that the optimum temperature is 425-450□. The percentage of product obtained when reaction mixture is at 425□ with 6 hours of reaction time was: ~1% solid residues, ~15% gaseous product, >80% was obtained as oil product, when the reaction was done at 500□ with 0.5hour of reaction time the percentage of products were: ~1% solid residues, ~22% gaseous products, ~77% oil product.

E. Comparison of Supercritical water Liquefaction and Thermal Pyrolysis

These studies when compared to the results of thermal pyrolysis indicated that the SWL method is much more efficient than the conventional thermal pyrolysis. In SWL method the precise optimum conditions were 450□ with reaction time of 1 hour which yielded 91% of the liquid product[16]..However, when the thermal pyrolysis was carried out by in presence of kaolin catalyst (optimum conditions: ~450 with catalyst: polypropylene ratio of 1:3)the optimal liquid yield obtained was 79.65% [11], in another study the thermal pyrolysis was done at ~500□ with variable increasing temperature rates (6-14□/min) and here the optimal yield was obtained at Temperature increasing rate of 6□/min with 82.12% of liquid product [17].

The efficiency and advantage of SWL method could be stated true due to following points:

1) The use of supercritical water may have improved heat and mass transfer due to high diffusion rates and low viscosity.
2) By using supercritical water, we potentially get a large operating window of temperature and other conditions to determine the exact optimum conditions required for better percentage of liquid products.
3) The SWL method is more eco-friendly as only supercritical water is being used,
4) The SWL method is much simpler to perform as compared to thermal pyrolysis.
5) Advantages of using supercritical water includes that water as a solvent is non-toxic, naturally occurring, non- flammable.
6) Water being cheap will make the overall process economical at a large industrial scale.

III.CONCLUSION

In view of increasing cases of COVID-19 and its mutants the rise for the use of PPE kits has also been increased. The conversion of these used PPE kits/masks and other products made from PP into useful biofuel would give solution to two major crisis problems i.e.

1) The disposal and dumping of PPE/masks/Toys leading to land pollution
2) Giving a new way to produce biofuels and slowdown the rate of exhaustion of the fossil fuels.

Out of the two methods discussed in this review article wiz. Conversion by pyrolysis with or without the presence of catalyst and conversion by means of supercritical water, the later was found out to be more eco-friendly method and gave out more oil product as compared to the former.

IV. ACKNOWLEDGEMENT

We are greatly indebted towards our teacher Mrs.Beena Negi for giving us an opportunity in elaborating our knowledge towards the subject (Green chemistry) by completing this review article and helped us to put our vague ideas in a concrete form. We are also grateful for our department for their constant guidance.

A. *Abbreviations*

1) *PPE:* Personal protection equipment
2) *PP:* polypropylene
3) *COVID-19:* Coronavirus disease of 2019.
4) *PTEG:* Polyethylene terephthalate glycol
5) *N95:* Filter standard used by US (Filters at least 95% of airborne particles)
6) *N99:* Filter standard used by US (Filters at least 99% of airborne particles)
7) *FPP:* Filter standard used for protective respirator masks certified by European Union
8) *FPP1:* 4-fold (Filters at least 80% of airborne particles)
9) *FPP2:* 10-fold (Filters at least 94% of airborne particles)
10) *FPP3:* 20-fold (Filters at least 99% of airborne particles)
11) *CPCB:* Central pollution control board
12) *ZSM-5:* Zeolite Socony Mobil–5**.**
13) *DCM:* Dichloromethane
14) *SWL:* Supercritical water Liquefaction.

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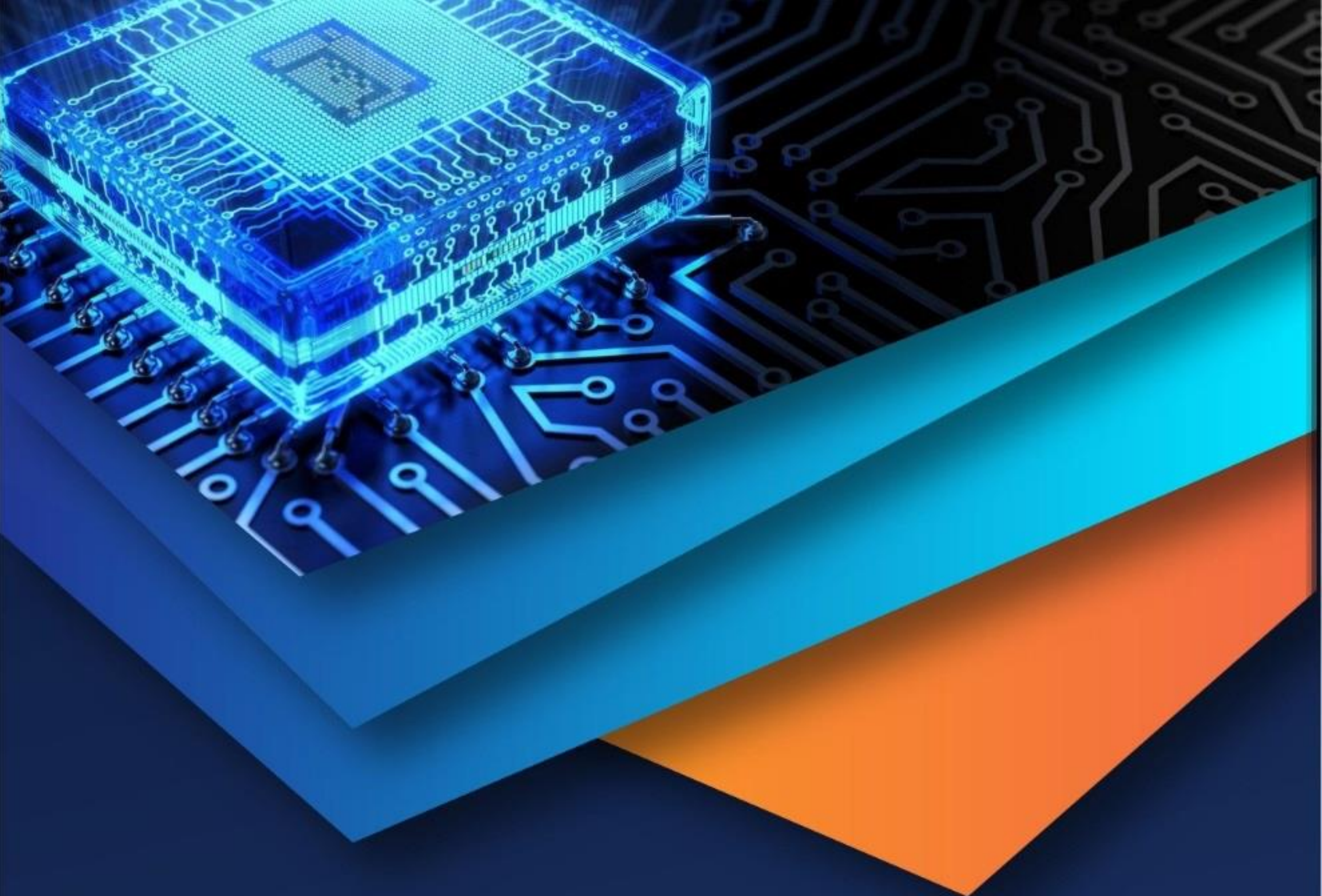

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