FORMULATION OF GREEN DIESEL BLENDS AND FINDING POTENTIAL CHEMICALS AS BIOFUELS USING COMPUTER-AIDED TECHNIQUE

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I dedicated this entire work to my beloved family, husband and daughter, who always be my side…

For all their selfless love, support, inspiration and encouragement

Thanks…

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LIST OF ABBREVIATIONS AND SYMBOLS

NOx	-	Nitrogen Oxide
CO_2	-	Carbon Dioxide
O_2	-	Oxygen
LA	-	Levulinic Acid
BL	-	Butyl Levulinate
CN	-	Cetane Number
DT	-	Distillation Temperature
GAMS	-	Generalized Algebraic Modeling System
ProPred	-	Property Prediction
ProCAMD	-	Computer Aided Molecular Design tool
ICAS	-	Integrated Chemical Aided Software
MPOB	-	Malaysian Palm Oil Board
ρ	-	Density
ν	-	Kinematic viscosity
PM	-	Particulate Matter
EFB	-	Empty Fruit Bunch
POME	-	Palm Oil Mill Effluent
MSDS	-	Material Safety Data Sheet

CAMD	-	Computer-Aided Molecular Design
NLP	-	Non Linear Programming

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CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter provides an overview of the research background about the energy demand and consumption in Malaysia, covering the alternative renewable energy sources, the dependency on fossil fuels, the advantages of biofuels and the production of biofuels from palm oil biomass. The research problem statement is then highlighted, followed by the objective and the scope of the study which is focused on finding the formulation of green diesel mixtures and the potential chemicals as biofuels from palm oil biomass. The chapter ends by describing the significance of the study followed by an overview of the thesis.

1.2 Research Background

Nowadays, biofuel from biomass has become an important alternative source of energy. Compared to fossil fuel, biofuel is almost totally CO_2 neutral and is therefore capable of reducing carbon dioxide emissions which is the main cause of global warming. Biomass-derived fuels also have negligible sulfur content and therefore, do not contribute to the emissions of sulfur dioxide which causes acid rain (Ashok, 2009). The production of biofuel from biomass also reduces the consumption of crude oil, thereby reducing dependency on fossil fuel.

According to estimates done by the International Energy Agency, a 53% increase in global energy consumption is foreseen by 2030, with 70% of the growth in demand coming from developing countries (Tick and Shing, 2010). Figure 1.1 shows the energy consumption by sectors in Malaysia. It shows that, transportation sector consumed almost 40%. Figure 1.2 shows the total energy demand in Malaysia. From Figure 1.2, oil is the most required/crucial/limited energy required in 2030. However, Malaysia is expected to become a net oil importer by 2030 and the Minister of Energy, Water and Communications stated that in 2006 ‘reserved of crude oil are projected to last for 19 years’ . It is a very crucial to find potential renewable energy technologies to fulfill the energy demand in Malaysia.

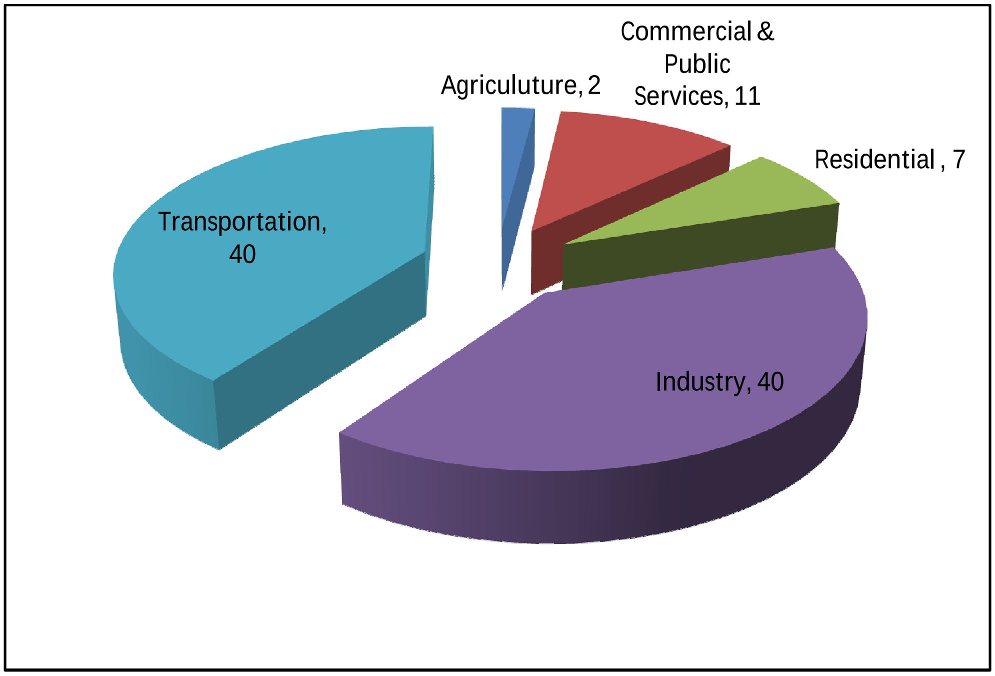

Figure 1.1: Energy Consumption by Sectors in Malaysia (Hugh Yard, 2008)

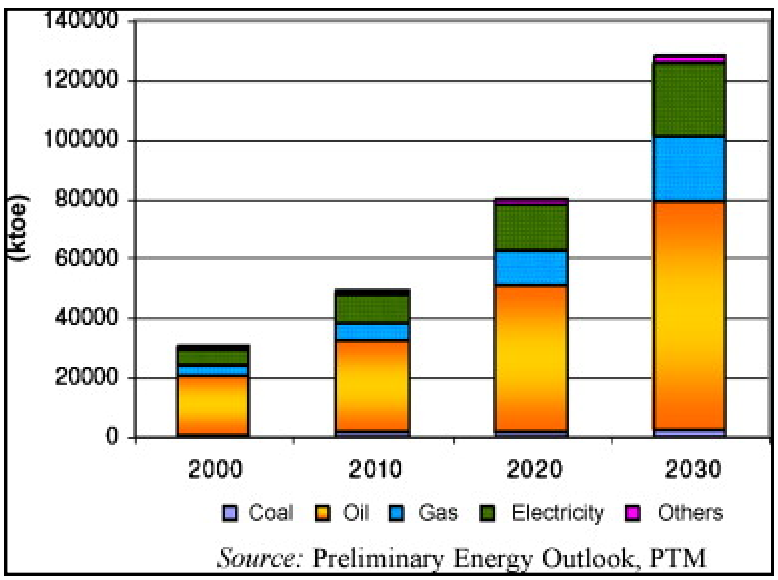

Figure 1.2: Total Energy Demand (Tick and Shing, 2010)

Transport worldwide consumes about one-fifth of global primary energy and is thus responsible for similar amounts of Green House Gas Emissions (Dirk and Nicklas, 2005). Table 1.1 shows the CO_2 emissions from fuel combustion. From the table, we can see that CO_2 emission from fuel combustion in Malaysia increased 235.6% from 1990 to 2009. This environmental problem leads government to consider sustainability as one of the goal for New Economic Model (NEM) Plan. The sustainability component of the NEM is meant to ensure that all of the proposed measures defined under the new model must be sustainable in both economic and environmental terms. Biofuel from biomass is one of the potential paths that are considered in order to achieve sustainability goals in the NEM.

Table 1.1: CO_2 emission from fuel combustion. (IEA statistic, 2011)

CO_2 emissions: Sectoral Approach

million tonnes of CO_2

	1971	1975	1980	1985	1990	1995	2000	2005	2007	2008	2009	% change 90-09
Non-OECD Total *	**4 204.1**	**5 379.0**	**6 795.9**	**7 667.5**	**9 194.8**	**9 414.1**	**10 033.8**	**13 168.7**	**14 850.7**	**15 607.5**	**15 939.0**	**73.3%**
Algeria	8.7	14.0	28.4	43.2	51.7	55.6	62.4	78.5	85.7	88.1	92.5	79.1%
Angola	1.7	2.0	2.7	2.9	4.0	4.0	5.1	7.0	10.4	12.2	12.9	222.1%
Benin	0.3	0.5	0.4	0.5	0.3	0.2	1.4	2.7	3.7	3.8	4.2	+
Botswana	..	..	..	1.6	2.9	3.3	4.2	4.4	4.4	4.5	4.2	42.5%
Cameroon	0.7	1.0	1.7	2.4	2.7	2.5	2.8	2.9	4.1	4.3	4.8	79.2%
Congo	0.6	0.7	0.8	0.8	0.7	0.5	0.6	0.9	1.2	1.5	1.7	138.1%
Dem. Rep. of Congo	2.5	2.6	3.1	3.2	3.0	2.1	1.7	2.3	2.6	2.8	2.9	-3.1%
Côte d'Ivoire	2.4	3.0	3.4	3.0	2.6	3.2	6.1	5.8	5.7	6.5	6.1	131.4%
Egypt	20.4	25.9	42.3	65.5	79.2	84.0	110.2	151.9	168.7	174.0	175.4	121.4%
Eritrea	..	..	..	..	..	0.8	0.6	0.6	0.5	0.5	0.5	..
Ethiopia	1.3	1.2	1.4	1.4	2.2	2.3	3.2	4.8	6.0	6.8	7.4	235.7%
Gabon	0.5	0.7	1.3	1.7	0.9	1.3	1.4	2.1	2.4	2.3	1.7	88.0%
Ghana	1.9	2.3	2.3	2.2	2.7	3.3	5.1	6.4	8.2	7.3	9.0	233.0%
Kenya	3.2	3.5	4.5	4.6	5.5	5.6	6.8	7.2	8.3	8.6	10.0	82.0%
Libyan Arab Jamahiriya	3.7	9.2	18.6	22.5	27.4	35.1	39.7	42.5	43.1	47.0	50.0	83.0%
Morocco	6.8	9.9	14.0	16.5	19.6	25.3	28.3	38.6	40.5	42.1	41.3	110.3%
Mozambique	2.9	2.3	2.3	1.5	1.1	1.1	1.3	1.5	2.1	2.0	2.2	106.8%
Namibia	..	..	..	..	..	1.8	1.9	2.9	3.3	4.2	3.7	..
Nigeria	5.9	11.7	26.7	32.4	29.2	31.1	39.4	50.4	44.1	49.6	41.2	41.3%
Senegal	1.2	1.6	2.0	2.1	2.0	2.5	3.6	4.6	5.0	5.1	5.3	161.4%
South Africa	173.8	209.2	214.5	229.1	254.7	276.9	298.2	330.3	356.5	388.4	369.4	45.0%
Sudan	3.3	3.3	3.7	4.2	5.5	4.6	5.5	10.0	12.0	12.1	13.3	140.9%
United Rep. of Tanzania	1.5	1.5	1.6	1.5	1.7	2.5	2.6	5.1	5.5	5.8	6.3	267.0%
Togo	0.3	0.3	0.4	0.3	0.6	0.6	1.0	1.0	0.9	1.1	1.1	97.5%
Tunisia	3.7	4.8	7.8	9.6	12.1	14.2	18.0	19.5	20.6	20.9	20.8	72.0%
Zambia	3.4	4.4	3.4	2.8	2.6	2.0	1.7	2.1	1.4	1.6	1.7	-34.9%
Zimbabwe	7.2	7.2	8.0	9.6	16.0	14.8	12.7	10.4	9.3	8.8	8.7	-45.9%
Other Africa	7.6	9.2	13.3	11.8	14.7	16.9	19.3	25.0	27.9	29.5	29.4	100.6%
Africa	**265.7**	**332.1**	**408.3**	**476.9**	**545.4**	**598.4**	**684.6**	**821.7**	**884.2**	**941.2**	**927.5**	**70.1%**
Bangladesh	3.2	4.7	7.2	8.8	13.6	20.5	25.3	36.5	42.0	46.4	50.7	273.5%
Brunei Darussalam	0.4	1.4	2.6	2.9	3.4	4.7	4.6	5.1	7.1	7.5	8.1	141.5%
Cambodia	..	..	..	..	..	1.4	2.4	3.7	4.4	4.6	4.3	..
Chinese Taipei	31.0	42.5	72.2	71.7	114.3	156.5	217.3	258.9	272.3	261.3	250.1	118.8%
India	200.2	241.2	283.3	411.0	582.3	776.6	972.5	1 160.4	1 357.2	1 431.3	1 585.8	172.3%
Indonesia	25.1	38.0	68.8	88.0	142.2	202.1	264.0	336.4	365.5	343.5	376.3	164.7%
DPR of Korea	67.5	76.7	105.6	126.4	114.0	74.9	68.8	74.3	62.4	69.4	66.2	-41.9%
Malaysia	12.7	16.1	24.2	33.4	48.9	78.5	111.1	152.8	171.3	181.7	164.2	235.6%
Mongolia	..	..	..	11.6	12.7	10.1	8.8	9.5	11.1	11.2	12.0	-5.3%
Myanmar	4.5	3.9	5.1	5.8	4.0	6.7	8.1	13.4	12.5	11.9	10.1	154.7%
Nepal	0.2	0.3	0.5	0.5	0.9	1.7	3.1	3.0	2.5	2.8	3.4	284.9%
Pakistan	16.6	20.9	26.1	39.1	58.6	79.5	97.3	117.2	138.6	133.0	136.9	133.7%
Philippines	23.1	29.1	33.3	28.6	38.1	57.0	67.9	71.3	68.9	71.0	70.5	85.1%
Singapore	6.0	8.4	12.7	16.3	28.8	37.5	40.2	44.1	45.6	46.1	44.8	55.7%
Sri Lanka	2.8	2.7	3.7	3.6	3.7	5.5	10.6	13.4	13.0	12.2	12.7	238.1%
Thailand	15.9	20.7	33.2	41.4	80.1	140.3	161.8	219.1	231.9	237.8	227.8	184.5%
Vietnam	16.1	16.7	14.8	17.1	17.2	27.8	44.0	80.8	93.1	102.1	114.1	563.2%
Other Asia	8.4	10.2	16.5	10.1	10.2	9.3	11.3	15.6	14.6	14.5	15.2	48.9%
Asia	**433.6**	**533.5**	**709.7**	**916.3**	**1 273.0**	**1 690.7**	**2 119.2**	**2 615.5**	**2 914.0**	**2 988.3**	**3 153.2**	**147.7%**
People's Rep. of China	800.4	1 051.2	1 405.3	1 704.9	2 211.3	2 986.1	3 037.3	5 062.4	6 028.4	6 506.8	6 831.6	208.9%
Hong Kong, China	9.2	10.8	14.5	22.0	32.8	36.0	39.8	40.7	43.4	42.2	45.6	38.9%
China	**809.6**	**1 062.0**	**1 419.8**	**1 726.9**	**2 244.1**	**3 022.1**	**3 077.2**	**5 103.1**	**6 071.8**	**6 549.0**	**6 877.2**	**206.5%**

* Includes Estonia and Slovenia prior to 1990.

According to Hugh Yard (2008), there are three ways to balance the energy budget. Firstly is by reducing consumption. Secondly is through better use of existing energy supplies. The last part is by utilizing alternative sources of energy. Palm oil biomass has a large potential as renewable energy sources. This is shown in Figure 1.3 in which, palm oil is estimated to supply about 38% of energy. The palm oil industry in Malaysia has grown to become the main agriculture-based industry. A lot of biomass by-product is produced from palm oil processing such as empty fruit bunch (EFB), palm oil mill effluent (POME), palm fibre and palm kernel shell. Cellulosic palm oil biomass (EFB, palm trunk, palm fiber) constitute a huge renewable resource that can be converted to chemical and fuel feedstocks. Palm oil biomass is one of the potential sources of biomass that can be used directly for energy or converted to more convenient transportable (liquid) fuels or transmitted energy (electricity) range.

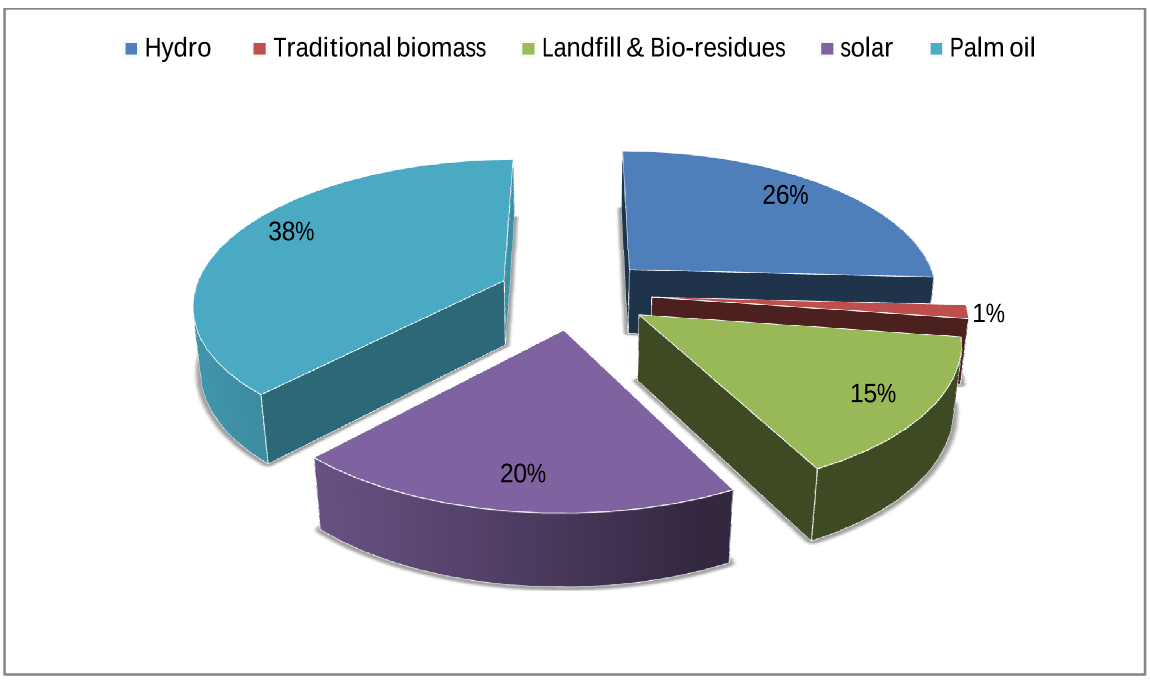

Figure 1.3: Estimated Renewable Energy Availability in Malaysia [Hugh Yard, 2008]

Biofuel is currently the most widely accepted alternative fuel for diesel engines due to its technical, environmental and strategic advantages. It has enhanced biodegradability, reduced toxicity and improved lubricity in comparison with conventional diesel fuels. Biofuel can be used pure or blended in existing gasoline and diesel engines without the need for significant modifications to the engine. Biofuel generally has higher density, viscosity, cloud point and cetane number, but lower volatility and heating value compared to commercial grades of diesel fuel (Grabosky M., 1998).

Biofuels have a lot of advantages. They are used to:

i) reduce the energy dependence of nations with respect to fossil resources acting as stabilizing factors in a global market environment.

ii) reduce the global pollution by less CO_2 emissions on a lifecycle basis.

iii) reduce the local pollution in terms of CO, CO_2, sulfur and particulate matters.

iv) enable recycling of various potentially energetic industrial and domestic wastes, such as cooking oil and fats, as well as agricultural residues.

v) ensure a better balance between industry and agriculture, create new jobs in rural areas and sustain economic growth.

1.3 Problem Background and Problem Statement

In order to have a smooth engine operation, it is important to use the right fuel blend ratio. There are various ways to determine the best blend ratio. Experimental methods for blending fuel at different ratios have been commonly used. The fuel blend is then tested and checked for performance as well as emissions. The fuel ratio that gives the best performance at low emissions will be selected as a good fuel blend. This method is however time consuming and costly because of the need to test many samples experimentally. Chemical product design using computer aided method to find the best ratio of fuel blend can save a lot of time and cost. Computer aided methods can significantly narrow down the search space to a number of feasible and promising candidates. Then, virtual experimental procedure can be conducted to verify the properties of the feasible shortlisted candidates and find the best fuel blend composition.

This study proposes two systematic methodologies. The first is to formulate diesel blended with biofuels including ethanol, butanol and butyl levulinate. General Algebraic Modeling System (GAMS) software was used to find the optimum blend composition. Pure component properties were extracted from CAPEC database. The second is to find potential chemicals as biofuels. Computer Aided Molecular Design tool (ProCAMD) was used as a tool to generate the potential candidates of chemicals that satisfy the target value of target properties.

Given a set of fuel property targets, it is desired to identify the formulation of feasible green diesel mixtures and the potential chemicals as biofuels. Computer aided molecular design (CAMD) technique was used as a tool to propose an economical and environmental friendly green diesel fuel.

1.4 Objectives of the Study

The main objectives of this research are described as below:

1. To determine the feasible fuel blend consisting of diesel and several candidates of biofuels using computer-aided techniques.

2. To develop a methodology for finding the potential chemicals to replace conventional biofuels for green diesel blend using (ProCAMD) as a tool.

1.5 Scope of the Study

Five main scopes have been identified to achieve the objectives of the study. These include:

i. Establishing the desirable target property values for the green diesel. The properties of the conventional diesel will be taken as target values to generate green diesel blends and to find feasible chemicals as potential biofuels.

ii. Developing a mathematical formulation to search for a set of feasible fuel blend compositions that satisfy the target properties of diesel standard using GAMS.

iii. Determining the formulation of the green diesel proposed based on cost and environmental factor.

iv. The cost of diesel and biofuels is based on current market. CO_2 emission reduction will be calculated based on the diesel emission factor and biofuel is assumed to produce zero carbon dioxide.

iv. Conducting virtual experiment using ASPEN PLUS as a validation step to check the miscibility of the green diesel mixtures.

v. Searching for chemicals with sustainable/green properties to replace conventional biofuels using ProCAMD as a tool.

vi. Analysin the potential routes to produce the chemicals identified in step v to ensure it can be produced from biomass.

1.6 Research Significance

This research provides an overview on the potential of biomass as the raw material to replace conventional biofuel.As a renewable material, palm oil has an important role to play in supplying the energy needs of the country by incorporating all its products into the national diesel supply. Its use as biofuel will create a new demand in the export market, thus helping to strengthen Malaysia's position as a leading producer and exporter of palm oil. It will also be in line with the global efforts to reduce the emissions of greenhouse gases, and underscores the Malaysia's contribution to this global objective. Utilization of biofuels is one of the ways to ensure adequate fuel supplies at a time when yields from existing oil fields are declining and new fields are not yet up and running. Biofuels can do much to help fill the gap between limited fuel supplies and increasing worldwide demand—a gap that is almost sure to widen in the coming years.

1.7 Research Contribution

There are four contributions of this study. They are:

i) A new methodology developed for the formulation of tailor-made green diesel fuels using computer-aided techniques.

A new methodology to search for feasible candidates of chemicals that have potentials as biofuels using computer-aided techniques.

ii) Formulations of green diesel blend that can reduce CO_2 emissions and sulfur contents.

iii) Candidates of biofuels that have properties similar to diesel and can be produced from lignocellulosic biomass.

1.8 Overview of the Thesis

This thesis consists of five chapters. Chapter 1 begins with the introduction of the research , the problem statement, the objectives and the scope of the studies which aims to find feasible fuel blends consisting of diesel and several candidates of biofuels using computer-aided techniques and to find potential chemicals that can be proposed as biofuels for green diesel blends.

Chapter 2 provides a review of the relevant literatures related to the scope presented in this thesis. Biofuels in diesel blends are reviewed. It also analyses the potentials of palm oil biomass as biofuels and technologies available to produce biofuels from lignocellulosic biomass. Important physical properties in diesel blends are also identified in order to choose the right target properties. Fundamental theory of computer aided molecular design (CAMD) is also discussed in this chapter.

Chapter 3 presents the detailed methodology of this study to achieve the targeted objectives. This chapter describes two new methodologies developed in this study. They are the development of the formulation of green diesel mixtures and the development of the methodology of finding potential chemicals as biofuels. Both methodologies are developed using computer aided technique. Besides that, this chapter also elaborates the procedure on virtual experiment as a validation step of the target properties using ASPEN PLUS as a tool.

Chapter 4 presents the results of the formulation of green diesel mixtures and the analysis of these results based on some criteria, such as cost, CO_2 emission and sulfur contents. There is also a list of chemicals that satisfies the target properties of diesel fuels. From the list, the chemical is analyzed whether might have potentials to be produced from lignocellulosic biomass. This chapter compares results of target properties from virtual experiments with the formulated green diesel mixture.

Lastly, Chapter 5 presents a summary of the study and some recommendations. These recommendations explore possible potential areas for future works.

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