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Preface

We would like to present, with great pleasure, the inaugural volume-6, Issue-1, January 2020, of a scholarly journal, *International Journal of Engineering Research & Science*. This journal is part of the AD Publications series *in the field of Engineering, Mathematics, Physics, Chemistry and science Research Development*, and is devoted to the gamut of Engineering and Science issues, from theoretical aspects to application-dependent studies and the validation of emerging technologies.

This journal was envisioned and founded to represent the growing needs of Engineering and Science as an emerging and increasingly vital field, now widely recognized as an integral part of scientific and technical investigations. Its mission is to become a voice of the Engineering and Science community, addressing researchers and practitioners in below areas

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Neural Networks	Plastic Engineering

Each article in this issue provides an example of a concrete industrial application or a case study of the presented methodology to amplify the impact of the contribution. We are very thankful to everybody within that community who supported the idea of creating a new Research with IJOER. We are certain that this issue will be followed by many others, reporting new developments in the Engineering and Science field. This issue would not have been possible without the great support of the Reviewer, Editorial Board members and also with our Advisory Board Members, and we would like to express our sincere thanks to all of them. We would also like to express our gratitude to the editorial staff of AD Publications, who supported us at every stage of the project. It is our hope that this fine collection of articles will be a valuable resource for *IJOER* readers and will stimulate further research into the vibrant area of Engineering and Science Research.

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Insight into Agricultural Mechanization in Cameroon: Case of Farm Operators, Users of Agricultural Equipment and Machines

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Abstract**—** *Cameroon has an economy strongly dominated by the agricultural sector and despite this domination as well as the fact that this sector is backed by several policy documents and statements, investments in the sector is still grossly underdeveloped. Many farm operators in the different agro ecological environment still rely to an overwhelming extend on the use animate power to achieve their agricultural production goals. This power source and the tools used have implicit limitation in terms of energy and operational output. Cameroon government persistently carry out some initiative to inverse the tendency such as the providing modern agricultural equipment and machinery to farm operators, training complex farm machinery users. However, these solutions are not part of a common though and so far have produced mixed results without a significant improvement on the field. This paper permits to appreciate the challenges faced by users of farm technology in agricultural mechanization via four main crops of significant importance to Cameroon: Maize, Cassava, Sorghum and Cocoa.*

Among others, it was observed that 75% of farmers involved in cultivation of sorghum, maize, cassava have land surfaces less than 2%. These small farm sizes are a serious handicap to the effective mechanization due to sparse and scattered cultivated lands. Also, only 13% (112) of farm operators have access to credit from micro finance institutions. This low access to credit contributes to the reluctance of farm operators to invest in agricultural machinery acquisition with only 3% owing a land with a land title.

Keywords**— *Adoption, Challenges, Farm operators, Insight, Mechanization.***

I. INTRODUCTION

Cameroon by its sociocultural diversity is a gift of nature, more so, in terms of agriculture and agronomy. It is characterized by a very dynamic population, a profusion of variety of crops that all do well throughout their respective agro-ecological zones, diverse climatic patterns suitable for various agricultural practices, just to name a few.

Agriculture (farming) is an activity carried out by a vast majority of Cameroonians (70%) with some enrolled in it as their main activity and others carrying it out as a secondary activity. Those that practice it as a main activity are organized as individuals or constituted in groups or associations with a common interest such as Common Initiative Groups, Cooperatives, etc. ([1] [2]).

However, animate power (human muscles or draft animals) constitute the main technology used to attain most of the agricultural objectives set by farm operators. Meanwhile mechanical power (internal combustion engines and/or electric motors) is still reluctant to dominate the agricultural field in Africa in general and in Cameroon in particular [3]. Agricultural mechanization is not an end in itself but a means that can help to bridge the gap that separates developed countries from agricultural developing countries sharing similar challenges like Cameroon [4].

According to [5], “Mechanization of agriculture and farming process connotes application of machine power to work on land, usually performed by bullocks, horses and other draught animals or by human labor.” This definition goes in straight line with [6], as ‘’it chiefly consists in either replacing, or assisting or doing away with both the animal and human labor in farming by mechanical power wherever possible”.

However, to make it more complete, the term agricultural mechanization equally embraces the manufacture, distribution and operation of all types of tools, implements, machines and equipment for agricultural land development and farm production as well as for harvesting and primary processing of agricultural produce [7].

Agricultural Mechanization is as such well placed to address most of the fundamental farming challenges in Cameroon in a profound manner. Indeed, agricultural Mechanization “removes the drudgery associated with agricultural labor, overcomes time and labor bottlenecks to perform tasks within optimum time windows and can influence the environmental footprint of agriculture leading to sustainable outcomes ([8] [9]).

The African Union Commission (AUC) and the Food and Agriculture Organization of the United Nations (FAO) view agricultural mechanization in Africa as an urgent matter and an indispensable pillar for attaining the Zero Hunger vision by 2025, as stated in the Malabo Declaration of 2014, Goal 2 of the Sustainable Development Goals, and the Prosperous Africa We Want, as indicated in Agenda 2063. Doubling agricultural productivity and eliminating hunger and malnutrition in Africa by 2025 will be no more than a mirage unless mechanization is accorded utmost importance.

However, the results of the current levels of commitment by various actors in Cameroon in order to promote agricultural mechanization still remain comparatively low. In fact, notwithstanding its fundamental importance and potentially beneficial role, Agricultural Mechanization is the neglected waif of agricultural and rural development in Cameroon ([7] [10]).

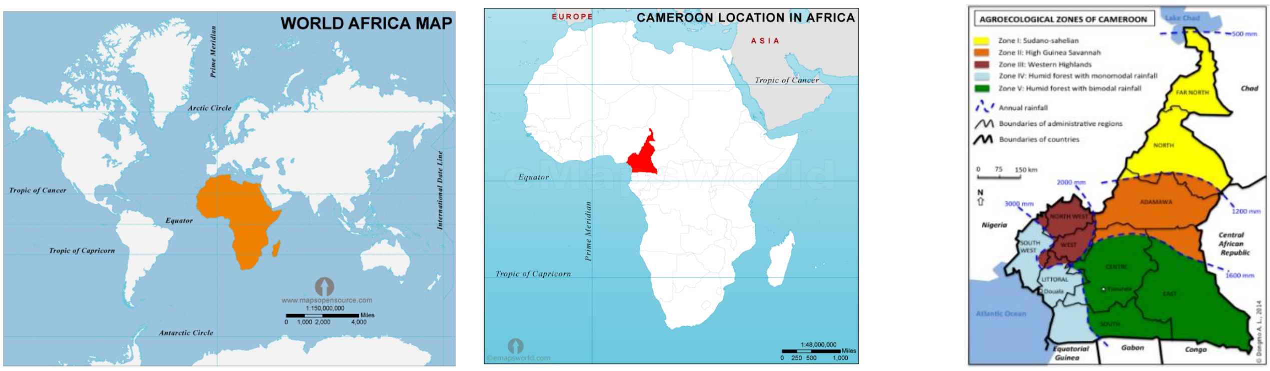
Increased agricultural production and improved rural livelihoods cannot be achieved without the adoption and use of increased levels of farm power and mechanization. However, agricultural mechanization is not quite as straightforward an input as fertilizer or seed; in order for farmers to have access to farm tools, machinery and equipment, there needs to be in place a whole complex system of manufacture, importation, retail outlets, support, provision of spare parts - the so-called supply chain - as well as the availability of advice and guidance for farmers (([11] [12]).

The purpose of this paper is to assess the situation of agricultural mechanization in Cameroon with a particular focus on the type of tools used currently by farm operators, the level of mechanization with regard to the importance of the power source and the various challenges that comfort the low adoption of agricultural mechanization.

II. METHODOLOGY

2.1 Description of the study area

Cameroon is a country located in Central Africa (Fig 1) with a total land area of 475,440 km2 and a population of about 24 million inhabitants [13]. It is bordered by Nigeria to the West, Chad to the Northeast, the Central African Republic to the East and Equatorial Guinea, Gabon, and the Republic of Congo to the South. Cameroon's coastline lies on the Bight of Bonny, which is part of the Gulf of Guinea and the Atlantic Ocean. Cameroon is sometimes described as "Africa in miniature," because it exhibits all the major climates and vegetation of the continent: mountains, desert, rain forest, savannah grassland, and ocean coastland. Cameroon can be divided into five agroecological zones (TABLE 1) distinguishable by dominant physical, climatic, and vegetative features. The climate varies with terrain, from tropical along the coast, to semi-arid and hot in the north. The coastal belt is hot and humid; it includes some of the wettest places on earth, such as Debundscha, located at the base of Mount Cameroon, which has an average annual rainfall of about 10,287 mm.



(a) Location of Africa in the world **(a) Location of Cameroon in Africa** **(c) Agro-ecological zones and administrative regions of Cameroon**

FIGURE 1: Presentation of Cameroon

Agriculture is the backbone of Cameroon's economy, employing 70% of its workforce and providing 44% of its gross domestic product and 30% of its export revenue. Cameroon produces several agricultural commodities for export and domestic consumption [14]. The most important of these, which vary by agroecological zone (TABLE 1), are cocoa, coffee, cotton, banana, rubber, palm oil, sugarcane, tobacco, tea, pineapple and peanuts for cash crops, and plantains, cassava, corn, millet, sorghum, yams, potatoes, sweet potatoes, dry beans, and rice for food crops. Animal husbandry is practiced throughout the country and is particularly important in the sahelian part of Cameroon.

TABLE 1
CHARACTERISTICS OF THE AGROECOLOGICAL ZONES

Agroecological zones	Surface Area (km^2)	Main crop and animal used for farm work
Sudano-Sahelian	100 353	Maize, millet-sorghum, rice, cowpea, soybean, onion, sesame, cotton, cattle, horses, donkeys
High Guinea Savanna	123 077	Maize, millet-sorghum, yam, cassava, sweet potatoes, rice, cotton, cattle, horses
Western Highlands	31 192	Maize, cocoa, beans, sweet potatoes, rice, Irish potatoes, ground-nuts, tomatoes, okra, sweet pepper, avocados, green vegetables, coffee, cassava, water melon
Mono-modal Humid Forest	45 658	Maize, banana, plantain, cassava, pepper, sweet potatoes, groundnuts, egousi, yam, vegetables, cocoa, coffee, oil palm, rubber
Bimodal Humid Forest	165 770	Maize, plantain, cassava, banana, cocoyam, cocoa, oil palm, rubber, coffee, maize, cocoa, oil palm, pineapples,

The study used both qualitative and quantitative methods in collecting and analyzing data. Quantitative methods formed the backdrop of the research while the qualitative data provided a detailed explanation of the findings.

2.2 Secondary data collection

This study started by a deep literature review of the records found within the Ministry of Agriculture and Rural Development (MINADER) which is the main institutional stakeholder that organizes, supports and accompany in various aspect other actors involved in agricultural mechanization such as farmer operators who are users of agricultural equipment and machinery, local agricultural equipment and machinery manufacturers, agricultural machinery suppliers, etc. Specifically, the secondary data were collected from projects and programs (under MINADER) that host the crops that were targeted for this study. However, documents from other ministerial departments with related competencies were scrutinized.

This permitted to identify all the stakeholders involved in the four (04) crops (maize, cocoa, cassava, sorghum) under investigation in agricultural mechanization as well as the role they play in this field but most importantly, it permitted to collect and appreciate data on previous level of mechanization of farm operators.

2.3 Primary data collection: sampling and target crops

Primary data collection was done through administration of questionnaire, interview and field observations. The questionnaire which was designed taking into consideration the various elements identified in the previous phase (literature review) as well as the specificities of the areas under investigation.

Four (04) crops were identified to assess the issues of agricultural mechanization in Cameroon (TABLE 2). These crops are very important for income generation and food security for the country but more precisely, maize was chosen because it is the most important (production and consumption) cereal crop in Cameroon, grown predominantly by smallholder farmers in the five agro-ecological zones of the country (TABLE 1). Cassava is one of the most important root crops in Cameroon. Cocoa is the main export commodities. Sorghum is the most important cereal grown in the northern Cameroon.

Their corresponding regions which were targeted for this study are among the main production basins of these crops.

TABLE 2
PRESENTATION OF CROPS AND REGIONS UNDER INVESTIGATION

Surveyed Region	Crop
West	Maize
Centre	Cocoa
South	Cassava
Far North	Sorghum

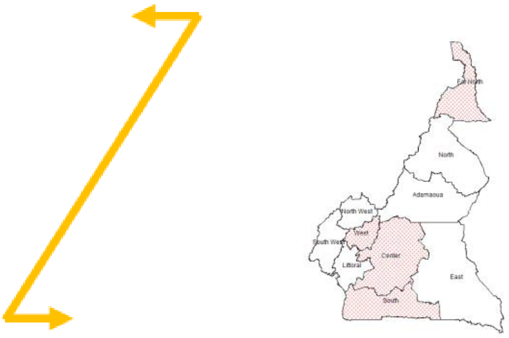


FIGURE 2: Mapping of surveyed regions

As highlighted in the introduction, more than 70% of the workforce in Cameroon is localized in the agricultural area, as such the population size of farm operators is significant. In order to collect qualitative data from the population and taking into consideration the important density of farm operators in rural areas, a sample size was calculated.

Simple random sampling was used to determine the sample size for this research. Due to the difficulty to have the exact population size, the researchers used 100,000 as the population size reason being that the sample size doesn't change much for populations larger than this figure.

$$Sample\ size, n = N * \frac{\frac{Z^2 * p * (1-p)}{e^2}}{[N-1+\frac{Z^2 * p\,(1-p)}{e^2}]} \tag{1}$$

Proposed by [15]

Where N = Population size; Z = Critical value of the normal distribution at the required confidence level (95%=1.96); p = Sample proportion (0.5); e = Margin of error (3%)

In order to increase the probability of collecting the maximum information, the responds rate was estimated at 90% to add on the total sample size a potential 10%. The data obtained from the survey research was compiled in an excel sheet and necessary filtration process was applied for further analysis.

III. RESULTS AND DISCUSSION

3.1 Sample size

In the four (04) regions surveyed, 865 questionnaires were filled among rural households from 186 subdivisions redistributed as presented on TABLE 3.

TABLE 3
SAMPLE SIZE PER REGION PER CROP UNDER INVESTIGATION

Region	Crop	Number of farm operators investigated
West	Maize	312
Centre	Cocoa	201
South	Cassava	108
Far North	Sorghum	244
Total		865

3.2 Farm sizes

According to CENEEMA and FAO (2011), the farming system in Cameroon is characterized by small farm operators who are found in majority and are involved in fair-trade average have farm sizes less than 2 hectares. About 20 years after, the reality is still the same. Indeed, the results from this survey showed that 75% of farmers involved in cultivation of sorghum, maize, and cassava have land surfaces less than 2%. A difference was observed for cocoa farmers that have relatively larger pieces of farmland because cocoa is a perennial crop own by the middle class population. It was found out that just 10% have land sizes less than 2ha, the largest proportion of farm operators in this field have farm sizes between 5 and 10 ha as presented in Fig 3.

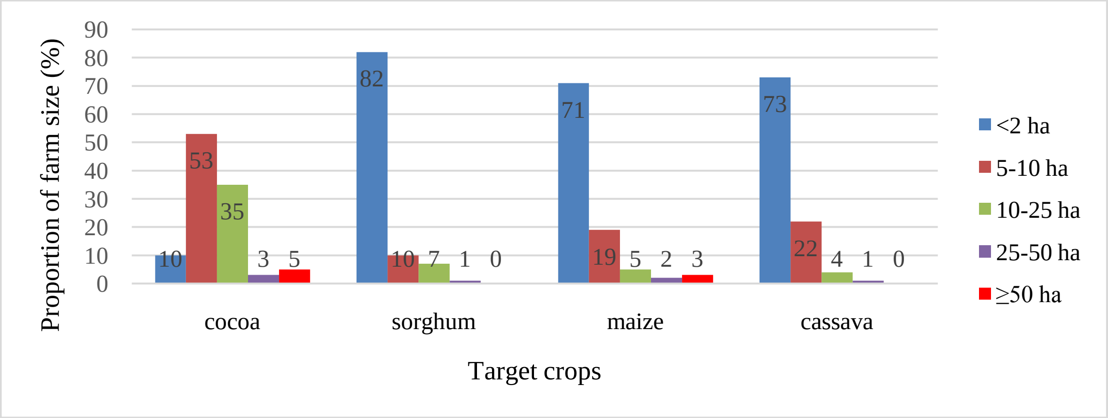


FIGURE 3: Farm sizes of farmers cultivating cocoa, sorghum, maize and cassava

These small farm sizes are a serious handicap to the effective mechanization due to sparse and scattered cultivated lands. In fact, the traditional cropping system is the legume-cereal rotation. Indeed, 80% of the farmers find it economically unsuitable to mechanize their farms regarding at the high cost of the modern agricultural equipment and machines compare to the farm output. Also, the quasi absence of specialized mechanization service providers makes it difficult for farm operations to be mechanized.

3.3 Access to credit and rural finance

The agricultural and rural sector is the driving force behind Cameroon's growth. Notwithstanding the fact that the fight against rural poverty is a national priority, its development is hampered by the limited access to financial services.

This research permitted to find out that the supply of financial services still remains very insufficient in rural areas, while the penetration rate of micro finance institutions, particularly among the poorest, especially women and young people, remains particularly low. The results of this surveyed showed that only 13% (112) of farm operators mostly constituted as farmer organization such as common initiative groups and cooperatives have access to credit from micro finance institutions. This low access to credit contributes to the reluctance of farm operators to invest in agricultural machinery acquisition.

3.4 Land tenure

In Cameroon, access to land title is a thorny issue as most farmers find it very difficult to access land titles. The study shows that 55% of farmers own their land without titles, while just 3% owns with title (Fig 4). Despite the fact that land titles can be obtained, the procedures are very lengthy and discourage several farmer operators. Also, cultural aspects such heritage makes land acquisition more complex as most families with a patriarchal background provide ownership to their descendants based on inheritance preferences. This point is worthy to highlight as most youths find themselves limited in the process of land acquisition thus, limiting farm mechanization. About 35% of farmers rents their land in order to overcome this issue of land tenure.

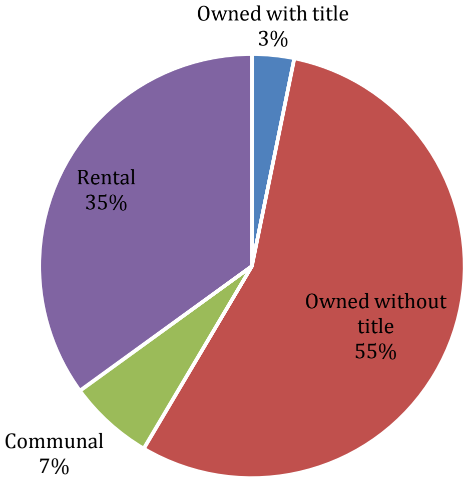


FIGURE 4: Land tenure ownership

3.5 Level of mechanization

Farm power is an essential input in agriculture for timely field operations for operating different types of farm equipment and for stationary jobs like operating irrigation equipment, threshers/shellers/cleaners/graders and other post-harvest equipment.

Despite some progress observed in the field of agricultural mechanization, this research showed that animate power is still very dominant in Cameroon. Indeed, manual tools constitute the essential tools used by farm operators regardless of the crop (under study) i.e. 89,8%. The tools used for draught animal farming are more dominant in the North Region of Cameroon than in the rest of the regions under investigation. However, they are timidly present in the West region (<1%). Motorization on the other hand, affects only 6.25% of farm operators (TABLE 4). From a global point of view, most of the modern tools used in specialized crop production can be identified on the field but their density, their frequency and quality of usage are still far from desired level.

TABLE 4
MAIN AGRICULTURAL EQUIPMENT AND MACHINES USED FOR FARM OPERATION AND POWER SOURCE

	Farm operation						
Crop	**Soil preparation**	**Planting**	**Plant control**	**Harvest**	**Transport**	**Conservation**	**Processing**
Maize	*Hoe *Cutlass *Tractor (+ plough; mower; harrow) *Rototiller (+plough) *Pair of oxen (+plough)	*Cutlass *Daba *Hoe *Tractor (+ cereal planter)	*Hand *Knapsack sprayer *Motorized sprayer *Fertilizer distributor	*Hand *Harvesters (+combine)	*Men's back *Wheelbarrow **Pousse pousse* *Tricycle *Motorcycle *Tractor (+ trolley) * Truck	*Cribs *Attic *On the ground *Biomass house dryers *Solar dryers	*Sheller *Mill
Power source		*manual (87%)*			*animal 1%*	*mechanical (12 %)*	
Cassava	*Hoe *cutlass *Tractor (+ plough;ridger; harrow)	*Cutlass *Hoe	*Knapsack sprayer *Motorized sprayer *Fertilizer distributor	*Hand *Digger *Cutlass	*Men's back *Wheelbarrow **Pousse pousse* *Tricycle *Motorcycle	*Nothing to report*	*Mill *Cassava press *Cassava graters
Power source		*manual (93%)*				*animal 0%*	*mechanical (7%)*
Cacao	*Axe *Cutlass	*Digger *Spade *Cutlass	*Knapsack sprayer *Atomizers *Pruner	*Cutlass	*Men's back *Wheelbarrow **Pousse pousse* *Tricycle *Moto *Tractor (+ trolley)	*Au sol *Dryer	*Pod breakers
Power source		*manual (96%)*				*animal 0%*	*mechanical4%*
Sorghum	*Hoe *Cutlass *Daba *Pair of oxen, horses or donkeys (+ plough)	*Cutlass *Daba *Hoe	*Hand *Knapsack sprayer *motorize sprayer	*Hand Knives (+Combine)	*Men's back *Wheelbarrow **Pousse pousse* *Tricycle *Motorcycle *Pair of animals with trolley	*Attic *On the ground *Storage rooms	*mill
Power source		*manual (83%)*			*animal (15%)*		*mechanical 2 %*

Very few Cameroon farmers own, share, or rent modern agricultural machinery. In terms of density of tractors per thousand hectares, Cameroon not only lags behind the developed countries but also behind some of the developing countries of the world.

It was found out that farm operators who invested in the purchase and use of high capacity machines and equipment exploit them for three main operations:

- Ploughing
- Sowing
- Harvesting

However, more than 70% of farm operators very desire to obtain modern and appropriate machines and equipment for complementary farm operation to increase not only their total production but also the quality of the end product, such as dryers for cocoa seed, cassava processing machines, maize electric dryers, hand driven motorized cocoa harvesters, cleaning equipment for sorghum; etc.

3.6 Degree of satisfaction of farm operators

When asked if farm operators were satisfied with the performance of their equipment, 74% of respondents clearly indicated that they were not satisfied. TABLE 5 presents the redistribution of the responses per region and per targeted crop. Among the most unsatisfied users are the farm operators from the North Region (93%), followed by the South Region (81%), Center and West Regions (68% and 61%).

TABLE 5
DEGREE OF SATISFACTION OF FARM OPERATORS

Region	Satisfied		Not Satisfied		Total	
	Number	*%*	*Number*	*%*	*Number*	*%*
Far North	17	7	227	93	244	100
Center	65	32	136	68	201	100
South	21	19	87	81	108	100
West	123	39	189	61	312	100
Total	226	26	639	74	865	100

Several reasons were given by users to justify their dissatisfaction. 51.05% cried the physical and financial inaccessibly to appropriate agricultural tools, equipment and machines; 40.95% mentioned the inadequacy of the equipment in relation to its conditions of use. Other reasons of noteworthy importance (8%) were also identified such as the absence of spare parts, the ageing of equipment, etc.

3.7 Possibilities of repair of agricultural machines and equipment

Correctly maintaining a tractor or agricultural machinery will add years to its useful life. Farm operators were asked on their possibilities to repair or have their equipment repaired. 71.35% of users of agricultural machinery and tools had the opportunity to repair them. On the other hand, 28.65% say they could not (TABLE 6). The high proportion of crude tools observed on the field, that can easily be repaired by local manufacturers could easily justify the high proportion of farm operators having access to maintenance and repair of their equipment.

TABLE 6
POSSIBILITY OF REPAIR OF AGRICULTURAL MACHINES AND EQUIPMENT

Region	Yes		No		Total	
	sample size	*proportion %*	*sample size*	*proportion %*	*sample size*	*proportion %*
Far North	169	69.3	75	30.7	**244**	100
Center	146	72.6	55	27.4	**201**	100
South	73	67.6	35	32.4	**108**	100
West	266	85.3	46	14.7	**312**	100
Total	**654**	75.6	**211**	24.4	**865**	100

3.8 Access to spare parts

Considering the simple type of equipment mainly used, spare parts do not constitute a handicap for users. As a result, 52.81% of respondents have no difficulties in finding spare parts (TABLE 7). It should also be noted that, with the exception of the Western Region, spare parts seem difficult to have for farm operators especially for modern complex tools.

TABLE 7
AVAILABILITY TO SPARE PARTS

Region	Availability to spare parts					
	Available		Not available		Total	
	sample size	*proportion %*	*sample size*	*proportion %*	*sample size*	*proportion %*
Far North	152	62.3	92	37.7	**244**	**100**
Center	84	41.8	117	58.2	**201**	**100**
South	36	33.3	72	66.7	**108**	**100**
West	183	58.7	129	41.3	**312**	**100**
Total	**455**	52.6	**410**	47.4	**865**	**100**

Most of the importer-suppliers are concentrated in two main cities (Regions) in Cameroon: Yaoundé (Center region) and Douala (Littoral region) having very few representatives in other Regions (production basins). A specific example is the case of EMEI Diesel who is the main importer supplier of agricultural machinery spare parts in Cameroon.

3.9 Possibility of training

More than 63.76% of farm operators don't have the opportunity to be trained in the use of their agricultural equipment (TABLE 8). This lack of opportunities is found in all regions of the country.

TABLE 8
POSSIBILITY OF TRAINING

Region	**Opportunity**		**No Opportunity**		**Total**	
	sample size	***proportion %***	***sample size***	***proportion %***	***sample size***	***proportion %***
Far North	76	31.1	168	68.9	**244**	**100**
Center	93	46.3	108	53.7	**201**	**100**
South	46	42.6	62	57.4	**108**	**100**
West	83	26.6	229	73.4	**312**	**100**
Total	**298**	34.5	**567**	65.5	**865**	**100**

However, the government shows clear willingness in assisting Cameroon Farm operators to not only adopt but equally, use modern adapted technology to become more competitive and contribute significantly to the achievement of food security (and sovereignty). Indeed, via some of the operational actors of the Ministry of Agriculture and Rural Development which are projects, the government provides training opportunities with specialized institutions on four wheel tractors driving and maintenance. This is the case of Agriculture Investment and Market Development Project (AIMDP), that has financed the training of 100 tractor drivers and mechanics from 45 farmer organizations mostly, farm cooperatives during 2019 on the best agronomic field uses and maintenance of tractors by the National Center of Studies and Experimentation in Agricultural Mechanization (CENEEMA) which is the only official institution in charge of farm operators training for various types of machinery use and maintenance.

3.10 Main challenges identified

The main challenges regarding agricultural mechanization as far as farm operators in various regions under investigation are concerned, were identified and are resume in Fig 5.

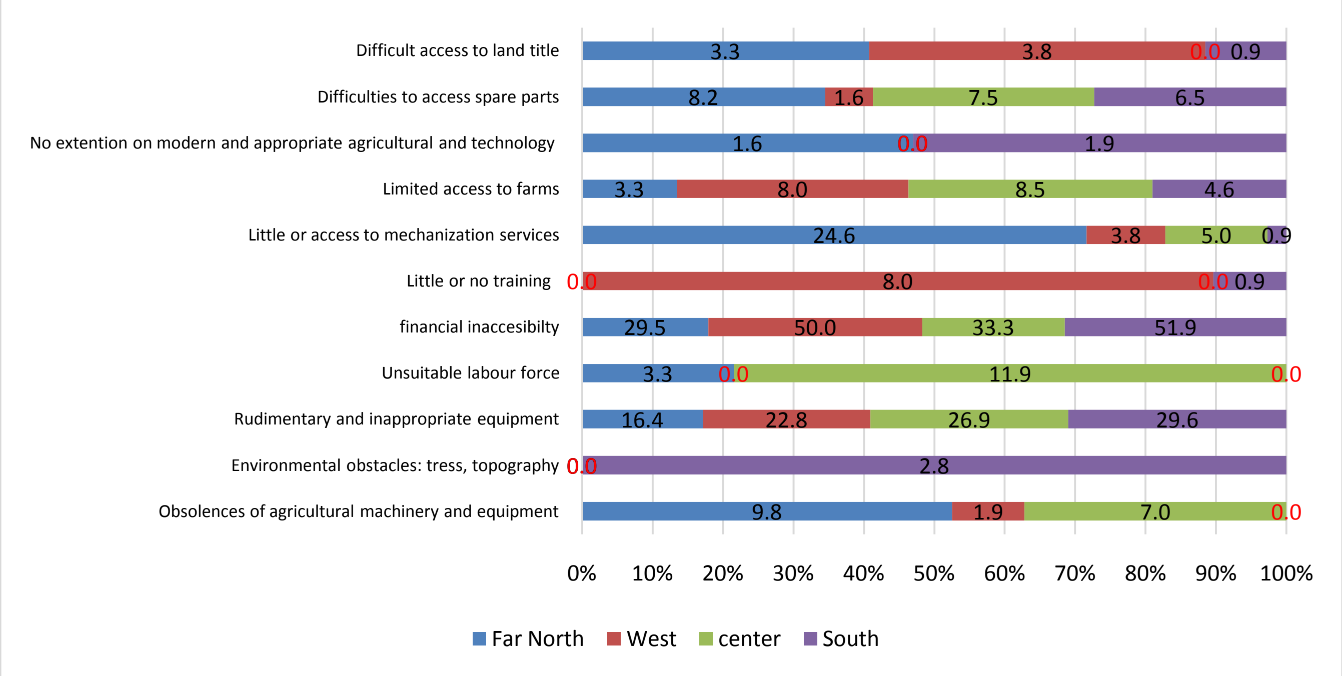


FIGURE 5: Main challenges of agricultural mechanization

The study shows clearly that the lack of institutions that finance agricultural activities is the main challenge for farmers in all the 04 regions (30% in far north; 50% in west; 33.3% in center and 51% in south). Secondly, the equipment used by farmers are inappropriate and rudimentary across the 04 regions of production (16% in far north; 23% in west; 27% in center and 30% in south), which undermine the productivity of the main crops. Hand tools are mostly used by farmers all over the country (FAO, 2001). The far north region has little access to mechanization services compared to the three other regions despite the presence of departments of agriculture. The difficulty to access the spare parts of machines is a great challenge for the 04 regions and need to be handled by private sectors, otherwise, machines will be abandoned after the first year of use. Ngu et *al.*, 2019, has proposed some solutions to better manage the hardware and software weaknesses of mechanical tool technology in agricultural mechanization.

IV. CONCLUSION

Controversy continues to surround the issue of mechanization, especially with regard to the level of mechanization appropriate to developing countries. However, few would deny that increasing agricultural productivity is the cornerstone of rural development. Despite this potential impact of mechanization, its adoption is still very difficult to achieve especially by small scale farmers due to the financial investment required. Farm mechanization in Cameroon has seen a rather slow progress over the years. The demand of important agricultural equipment like tractors, power tillers, combine harvesters, irrigation pump sets, diesel engines, has shown an increasing trend. This paper permit to appreciate the situation of agricultural mechanization in Cameroon via four (04) main crops.

Indeed, it was observed that the farming system in Cameroon is characterized in a majority (75%) by small farm operators with farm sizes less than 2 hectares. Significant farm sizes were observed from farmers that farm cocoa. Also, it was found out that 55% of farmers own their land without titles, while just 3% had land titles.

Despite some progress observed in the field of agricultural mechanization, this research showed that animate power is still very dominant in Cameroon. Indeed, manual tools constitute the essential tools used by farm operators regardless of the crop (under study) i.e. 89,8%. Motorization on the other hand, affects only 6.25% of farm operators. Also, 74% of farm operators are still not satisfied with the type of tool or technology they use to achieve their agricultural production goals. The main reasons for these dissatisfactions are the physical and financial inaccessibly to appropriate agricultural tools, equipment and machines; the inadequacy of the equipment in relation to its conditions of use; the absence of spare parts, the ageing of equipment, etc.

This work permits to appreciate the current state of mechanization from four main crops with the various challenges faced by the users of farm technology which if tackled efficiently could significantly improve the impact of mechanization in Cameroon.

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Analysis of the Plate Heat Exchanger Failure

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***Abstract*— *The present article describes the effect of the pressure on the operability of the plate exchanger of the SWEEP IC 5 x 20 type as well as the results of the numerical analysis of the stresses at three different loads. The exchanger was tested at the testing pressure defined by the manufacturer (2 MPa). Maximum stresses were observed at the places of soldered joints on individual exchanger plates and the stress was highly above the carrying capacity of the solder joint. With an increasing distance from the place where the boards were connected, stress exhibited a sharp increase. The testing was also focused on the stresses on the surface area (shroud) of the exchanger at the permissible operating pressure of 1.6 MPa defined by the manufacturer. An important observation was the stress identified at the measured real operating pressure of 0.7 MPa –destruction of the exchanger used by the operator.*

***Keywords*— plate heat exchangers, numerical analysis of stress.**

I. INTRODUCTION

The supply of heat via heat distribution systems may be accompanied with failures of plate heat exchangers which may occur in the following two cases:

1) At the formation of the total hydraulic impact in the system when the pressure in the conveyed fluid exceeds the permissible value of the stress in the material of the soldered joint;

2) If there is a hidden defect in the exchanger which is detected during the exchanger operation.

The article presents the case of analysing the plate heat exchanger destruction which occurred during the unsteady flow of water in the distribution system, characterised with time changes in the flow rate and pressure of water. Such unstable condition may be induced by various causes, most frequently by a failure of the pump or a sudden opening or closing of the regulating element in the pipeline during the steady flow of the fluid from the heat exchanger to a consumer. The shorter the time of closing the valve, the higher the proportion of kinetic energy of water transforms into the deformation work, and the more intensive the exerted hydraulic impact force in the system [1], [2], [3]. The intensity of the hydraulic impact may be one of the causes of the failures of the inner and outer walls of the exchanger, as shown in Fig. 1 and Fig. 2.

FIGURE 1: Deformation of the outer wall of the exchanger

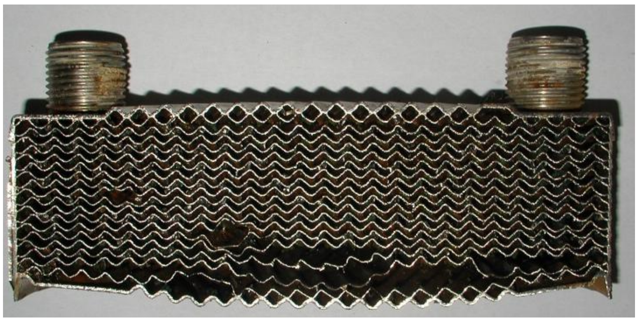

FIGURE 2: Deformation of the soldered joints of boards

II. ANALYSIS OF HYDRAULIC IMPACT

The outer smoother plate (shroud) of the analysed plate heat exchanger was 1.3 mm thick. This parameter of the exchanger plate was measured after the destruction thereof during the operation (Fig. 2). The inner profiled heat-transfer surface of the plate was 0.43 mm thick. The values required for the identification of an increase in the pressure in the distribution system were obtained by measuring the volumetric flow rate of water in the heat distribution system Q_V and subsequent analytical calculations. Table 1 contains the parameters corresponding to the water with the temperature of 55 °C.

The calculations were made using the following formulas:

$$\Delta p = \rho \cdot \kappa \cdot a_{\text{theor}} \cdot \upsilon \text{ (Pa)} \tag{1}$$

Where ρ is the density of water at the given temperature of water ($\text{kg} \cdot \text{m}^{-3}$); υ is the water flow velocity ($\text{m} \cdot \text{s}^{-1}$); a_{theor} is the theoretical speed of sound in the fluid ($\text{m} \cdot \text{s}^{-1}$); and κ is the pipeline elasticity coefficient (1).

The theoretical speed of sound in the fluid is calculated using the following formula:

$$a_{\text{theor}} = \sqrt{\frac{K}{\rho}} (\text{m} \cdot \text{s}^{-1}) \tag{2}$$

Where K is the volume modulus of elasticity of the fluid (for water it was $2.3 \cdot 10^9$ Pa).

The pipeline elasticity coefficient κ was identified using the following formula:

$$\kappa = \frac{1}{\sqrt{1 + \frac{K \cdot d_1}{E \cdot s}}} \tag{3}$$

Where E is the modulus of elasticity of the pipeline material (for steel pipes it was $2.1 \cdot 10^{11}$ Pa); d_1 is the external diameter of the pipeline; and s is the thickness of the pipe wall.

The real speed of sound in water was calculated as follows:

$$a_{\text{real}} = \kappa \cdot a_{\text{theor}} (\text{m} \cdot \text{s}^{-1}) \tag{4}$$

TABLE 1
PARAMETERS REQUIRED TO EXPRESS INCREASED PRESSURE IN THE DISTRIBUTION SYSTEM

ρ ($\text{kg} \cdot \text{m}^{-3}$)	a_{theor} ($\text{m} \cdot \text{s}^{-1}$)	κ (1)	a_{real} ($\text{m} \cdot \text{s}^{-1}$)	Q_V ($\text{m}^3 \cdot \text{s}^{-1}$)	υ ($\text{m} \cdot \text{s}^{-1}$)	Δp (MPa)
988	1,525.8	0.9756	1,488.6	0.00015	1.3263	**1.9505**

The length l of the circulation pipeline (from the heat exchanger to the customer) was 22.4 m. The blast (shock) wave would pass this route from the valve to the exchange, where it expands, in the time $t = l/a_{\text{real}} = 0.015$ s. The time in which the shock wave returns back to the place where it began, i.e., to the regulating element, was $T = 2 \cdot l/a_{\text{real}} = 0.030$ s.

The pressure in the supply pipeline of the distribution system was scanned using the ALMEMO MA 2390-8 measuring device by AHLBORN equipped with the FD 8214 17U pressure sensor and with the measuring range from 0 to 10 MPa. This device applied the pressure scanning frequency with the sampling frequency of 10 data per second. When investigating the presence of the total hydraulic impact in the given circuit, the used device for measuring the pressure is able to detect only a partially damped shock wave of such impact.

The values of the pressure p measured during the morning peak hours at the outlet from the exchanger ranged from 0.44 MPa to 0.59 MPa. During the evening peak hours, the pressure ranged from 0.44 MPa to 0.61 MPa.

The total increase in the pressure in the system Δp_{tot}, at a measurable pressure increase in the distribution system at the outlet from the heat exchanger, may be expressed as the pressure in the circulation pipeline p, increased in the value of the pressure Δp which may occur during the hydraulic impact, as follows:

$$\Delta p_{\text{tot}} = p + \Delta p \text{ (Pa)} \tag{4}$$

The manufacturer of the analysed exchangers tests their performance at the maximum pressure of 2.0 MPa and the permissible operating pressure of 1.6 MPa. The distribution system into which the exchanger was incorporated exhibited the deformation of the soldered joints of the inner plates of the exchanger at the operating pressure of only 0.7 MPa. The numerical calculation of the stress in the analysed plate exchanger was therefore made applying this particular pressure as the boundary condition.

During the measurable partial hydraulic impact, the pressure in the system increased in $\Delta p = 1.9505$ MPa. At the pressure in the system, for example, during the evening peak hours, with the value of 0.61 MPa, the total pressure of water in the system would be approximately 2.56 MPa; this exceeds the value of the testing pressure defined by the manufacturer in approximately 28 %.

The SWEEP IC 5 x 20 exchanger was analysed applying numerical mathematical methods in the COSMOS/M and ANSYS_10.0 environments [4], [5]. The boundary condition for the analysis of the stresses in the body of the exchanger was the pressure acting on the inner wall of the exchanger shroud, as shown in Table 2.

TABLE 2
BOUNDARY CONDITIONS OF THE ANALYSIS

Maximum testing pressure defined by the manufacturer (MPa)	**Permissible operating pressure defined by the manufacturer (MPa)**	**Pressure during the real operation of the exchanger (MPa)**	**Measured deformation of the shroud δ (mm)**
2.0	1.6	0.7	10.5

The calculation was made using the maximum testing pressure defined by the manufacturer, i.e., 2.0 MPa, and the permissible operating pressure, i.e., 1.6 MPa. Subsequently, the exchanger was tested for the condition corresponding to the real plastic deformation of the front external wall of the exchanger (Fig. 1). This deformation was identified on the basis of the measurement of the deformed exchanger and represented the value of 10.5 mm. It was detected by the operator during the real operation of the exchanger at the pressure of 0.7 MPa.

III. VERIFICATION OF THE STRESSES IN THE SWEEP IC 5 X 20 EXCHANGER

The basic parameters of the tested exchanger were: height – 190 mm; width – 73 mm; thickness of the inner heat-transfer surface 0.43 mm; thickness of the external plate – 1.3 mm; material – unknown nickel alloy; testing pressure – 2.0 MPa; permissible operating pressure – 1.6 MPa; and pressure during the real operation of the exchanger – 0.7 MPa.

The calculation of the stress was made for the area of linear and non-linear statics. The stress analysis in the area of the linear statics was performed applying the following boundary conditions: pressure on the inner side of the exchanger plate $p = 2$ MPa and 1.6 MPa; modulus of elasticity of the material $E = 2.1 \cdot 10^5$ MPa; and Poisson's ratio $\mu = 0.3$. For the non-linear stress analysis, the boundary conditions were as follows: pressure on the inner side $p = 0.7$ MPa; modulus of elasticity of the material $E = 2.1 \cdot 10^5$ MPa; and Poisson's ratio $\mu = 0.3$. For each calculation, the exchanger plate was fixed along its edges, in the openings of the water inlet and outlet on the exchanger, and at the points of soldered joints where the deformation was hindered in all directions ($x = y = z = 0$). With regard to the shape of the exchanger, the analysis was performed as a symmetrical task. The result of the stress analysis of the heat exchanger was the information on the *stress distribution* across the exchanger shroud and the *deformation extent* at individual loads.

At the *testing* pressure of 2 MPa, maximum stresses were formed at the points of soldered joints on individual exchanger plates. As the distance from the plate joints increased, the stress sharply increased as well. At the given pressure, the peak stress σ reached the value of as much as 425 MPa (Fig. 3).

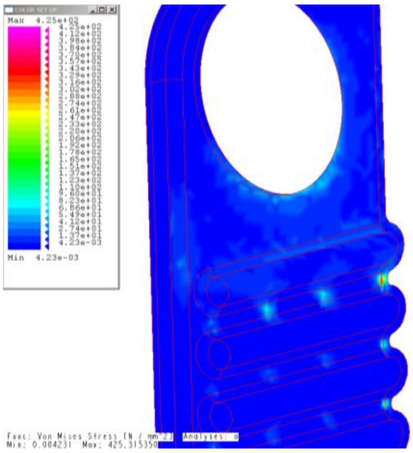

FIGURE 3: Detail of the stress distribution in soldered joints (p = 2 MPa)

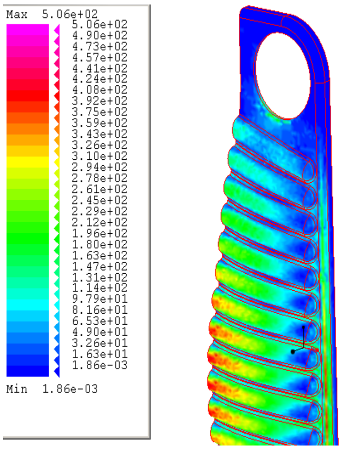

FIGURE 4: Stress distribution on the external wall (p = 1.6 MPa)

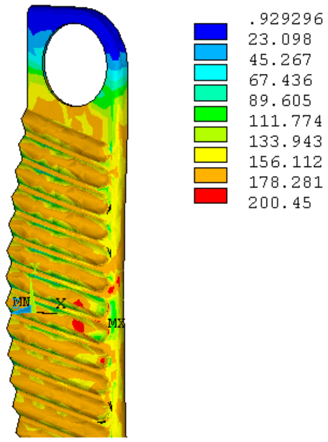

FIGURE 5: Stress distribution on the external wall (p = 0.7 MPa)

At the *permissible* operating pressure declared by the manufacturer (1.6 MPa), the stress was observed on the surface area (shroud) of the exchanger. The maximum stress σ on the wall reached the value of as much as 506 MPa (Fig. 4).

At the *measured* operating pressure of 0.7 MPa, the stress was observed in the area of the non-linear statics. For the available solders, the distribution of the yield stress values ranged from Re = 170 MPa to Re = 1,030 MPa. Due to unknown physical properties of the used solder, the calculation of the yield stress was made on the basis of the known deformation of the exchanger wall representing 10.5 mm. The approximation method of calculation, with the known value of the deformation of the exchanger front plate, the corresponding value of the yield strength was identified as 178 MPa. This value was affected by the number of kinematic reinforcements. The given value of the yield strength corresponds to the NICOLOY 800HT solder material. With this material and at the pressure of 0.7 MPa, the stresses in the top plate of the exchanger are shown in Fig. 5. The maximum stress σ on the exchanger plate achieved the value of 200 MPa.

On the basis of the performed calculations and analysis it is possible to state that the design stress in the walls of the front and rear plates of the exchanger must not exceed the following value:

$$\sigma_{\mathrm{D}} = \frac{\mathrm{Re}}{1.5} = \frac{178}{1.5} = 115\ \mathrm{MPa} \tag{5}$$

Corresponding to the design pressure p_{d} of 0.47 MPa. The constant 1.5 represents the safety criterion. Once this value is exceeded, plastic deformation gradually develops in the exchanger plates and the exchanger loses its function.

IV. CONCLUSION

Provided that the soldered joints exhibit full and functional carrying capacity, the exchanger may be pressurised up to the value of $p = 2$ MPa. At such pressure, the walls of the front plate are exposed to the stress σ of only 10 MPa which is sufficiently below the permissible value $\sigma_{\mathrm{P}} = 115$ MPa. All the primary forces are then transferred through the soldered joints. Therefore, the exchanger components that are loaded the most are the soldered joints. The exchanger works reliably until these joints are destructed. The soldered joints become destroyed, and hence the exchanger losses its function, in the following two cases:

1) A sudden increase in the pressure in the exchanger above the carrying capacity of the soldered joint;
2) Due to the effects of the cyclic fatigue life of the soldered joint which gradually loses its carrying capacity due to the cyclic loading, and after the material reaches its kinetic carrying capacity, the joint becomes destructed and the exchanger walls gradually experience plastic deformation. This is a well-known correlation between the “stress (force) and the number of cycles” equal to the fatigue life.

Reliable operation of SWEEP exchangers, IC 5 x 20 types, depends on the carrying capacity of the soldered joints. As operators cannot affect this qualitative property of the exchanger, the problem of exchanger deformation, with the given solder material and during the operations at pressures above 0.47 MPa, must be addressed by the manufacturer.

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Immobilization of commercial lipase onto different supports: characterization and application in esterification reaction

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Abstract— *The current preference of costumers for natural and healthy products is increasing the employment of biotechnological processes that use enzymes, and the synthesis of esters is an example of this change. However, enzymes are high-cost product, which stimulates research in finding solutions that make them more economically attractive, like immobilization. This work aimed to use different protocols for immobilizing lipase and its application in ester synthesis. The results showed that Pseudomonas fluorences lipase (AKL) was the most efficient for immobilization among other studied lipases (Pseudomonas fluorences lipase (AKL), Pseudomonas cepacia lipase (PSL), Hog Pancreas lipase (PHL), Pancreas Porcinas lipase (PPL), and Mucor Javanicus lipase (MJL)), with hydrolytic activity of 3323.6 U/g. Both immobilization methods (physical adsorption and entrapment) showed promising results towards hydrolytic activity. The best immobilization by adsorption was obtained using AKL onto PHB (polyhydroxybutyrate), with 698.61 U/g of hydrolytic activity. For entrapment, AKL also presented the best result, with 247.30 U/g of hydrolytic activity. For the synthesis of ester, after a 60 h-reaction using the immobilized derivatives by physical adsorption, the esterification yield was 74.26 %. In terms of hydrolytic activity, the employed protocols were very promising and encourage the continuity of this study towards the optimization of processes using industrial lipases.*

Keywords*— *Adsorption, Entrapment, Lipase, Ester, Hydrolysis.

I. INTRODUCTION

In the drive for alternative solutions for production, reduction of costs, and application of environmental friendly production, the replacement of chemical catalysts for biological catalysts has been growing over the time due to the attractive characteristics of enzyme for industries, such as: high specificity an selectivity, low toxicity, purity of the product, reduced environmental impact, easy handling, reducing energy cost by lowering the process temperature, use of mild pH values, among others [1,2,3]. Even if the enzyme demand is high, not all types of enzymes are produced in industrial scale because of the difficulty in finding high yield, activity, and stability enzymes [4].

In order to bypass the difficulties of using enzymes industrially, the development of immobilization techniques revolutionized and expanded the employment of enzymes, because the immobilization process allows them to be reused many times [5]. The most known and applied immobilization methods are: covalent binding [6], physical adsorption [7], entrapment (or encapsulation) in polymeric matrix [8], reticulation [9], and bio selective adsorption [10].

The entrapment of enzymes in porous matrices promotes the creation of a protector microenvironment for the enzymatic structure, which improves its operational stability [11]. The pores formed in the enzyme-support complex allow small molecules to diffuse easily and reach the active site of the entrapment enzyme, which enables it to keep its activity even after immobilization [8]. In physical adsorption, the molecules of enzyme adhere to the support surface through hydrophobic interactions, and, because of that, the adsorbed enzymes usually are resistant to proteolysis and aggregation [12, 13].

Lipases, formally named as triacylglycerol hydrolases (E. C. 3.1.1.3), consist in a class of hydrolytic enzymes of great applicability as biocatalyst in various reactions, such as esterification and transesterification [14]. They act on hydrolysis of oils and fats, releasing fatty acids and glycerides in the presence of water. Lipases can be obtained from vegetal or animal tissues, or from microorganism cultivation [15]. They present attractive aspects for industrial application such as: easy modification of catalytic properties that could be shaped through changes in its genetic structure, or reaction conditions; high specificity; and high enantioselectivity, which makes it to be used in organic synthesis [16, 17, 18].

Among many applications for lipase, the synthesis of esters via enzymatic reaction is growing due to the increase of interest *in natural* products in food industry. Esters (RCOOR') are organic compounds well distributed in nature. Glycerin esters are called glycerides, and they form the main oils and fats. A lot of simple esters are liquids with pleasant scent, responsible for fruits and flowers aromas. Those short chain esters have great industrial application as flavoring agents, besides their presence in fermented beverages [19]. Some aromatic esters of short chain fatty acid and alcohols are great value compounds for fragrance in food industry. That is why some authors study the direct esterification of fatty acids and alcohols in a non-polar media using free or immobilized lipase as biocatalysts [20, 21, 19].

In this work, different supports were used to immobilize commercial lipases from microbial and animal sources by physical adsorption and entrapment, applied in hydrolysis and esterification reactions.

II. MATERIALS AND METHODS

2.1 Lipases, supports and reagents

The commercial lipases used in this work (*Pseudomonas fluorences* (AKL), *Pseudomonas cepacia* (PSL), *Hog Pancreas* (PHL), *Porcine Pancreas* (PPL), and *Mucorjavanicus* (MJL)) were acquired from Sigma Co, USA. Chitosan (chit) *in natura*, polyhydroxybutyrate (PHB), and sodium alginate were commercially obtained and used as support for immobilization.

Other reagents used were: solvents (acetone, ethanol); salts (dehydrate calcium chloride, sodium chloride, dibasic potassium phosphate, monobasic potassium phosphate); emulsifiers (gum arabic); alkali (sodium hydroxide). The reagents used were of analytical grade, and purchased from Synth. Specific reagents, such as: bovine serum albumin (BSA) and Coomassie Brilliant Blue G-250, were acquired from Sigma Co, USA.

2.2 Support treatment for physical adsorption

At first, chitosan and PHB *in natura* were soaked in ethanol 95% w/w, and kept at rest at room temperature for 2 h(hours)[22]. Thereafter, the support was vacuum filtered and washed with distilled water.

2.3 Lipase immobilization by physical adsorption

An amount of 10 g of pre-treated support was added to 190 mL of enzymatic solution with initial protein loading of 5 and 10 $mg/g_{support}$. This system was incubated for 8 h, at 125 rpm, and room temperature (around 25 °C). At the end of the process, the immobilized derivative was vacuum filtered, washed with distilled water, and stored for drying.

2.4 Lipase immobilization by entrapment (hydrogel)

Two lipase solution was prepared (5 and 10 mg/mL), and also two $CaCl_2$ solution (0.1 and 0.2 mol/L). 0.5 g of sodium alginate was dissolved in 10 mL of each lipase preparation, and afterwards, lipase solution was slowly trickled into sodium alginate solution. By doing this, the lipase solution is converted into sodium alginate small spheres. Those spheres were vacuum filtered and washed with a known volume of distilled water. This filtered was analyzed for protein content and hydrolytic activity as well as the washing water.

For both immobilization protocols, the evaluation of immobilization procedure was measured by immobilization yield (IY) according to Eq. (1).

$$IY(\%) = \frac{P_t}{P_0} * 100 \tag{1}$$

Where P_t is the concentration of residual protein after an incubation time (mg/mL), P_0 is the initial concentration of protein (mg/mL).

2.5 Protein Determination

The concentration of protein from commercial enzymes preparation was evaluated in duplicate by Bradford method [23], which is based on the binding of Coomassie Brilliant Blue G-250 dye to the protein chain. Bovine serum albumin was used as a standard to construct the calibration curve between 0 and 0.9 mg/mL. The reading was obtained in spectrophotometer at 595nm.

2.6 Hydrolytic Activity

The hydrolytic activity of the immobilized enzyme was measured by titration method through hydrolysis of olive oil [24]. The substrate was an emulsion of Arabic Gum at 7% (w/v) and olive oil in a proportion of 50% (v/v), and the reaction mixture was composed by 5 mL of substrate, 4.9 mL of sodium phosphate buffer (0.1 mol/L, pH 7.0), and 100 µL of enzyme solution or 100 mg of immobilized enzyme (dry weight) placed in a 125 mL erlenmeyer flasks. The flasks were incubated in a water bath shaker with controlled temperature at 37 °C under continuous agitation at 200 rpm for 5 min. After this time, the reaction was stopped by adding 10 mL of acetone and ethanol mixture 1:1 (v/v), and the free fatty acids were titrated with NaOH 0.02 mol/L standard solution using phenolphthalein as indicator. According to the consumed volume in titration, it was possible to calculate the hydrolytic activity of free and immobilized lipase from Eq. (2), considering that one unit of activity corresponds to the amount of enzyme required to release 1 µmol of fatty acid per minute of reaction at test conditions. The results were expressed as U/g.

$$HA = \frac{(Vb - Va) * 1000 * M}{t * m \text{ or } v} \tag{2}$$

Where HA is hydrolytic activity (U/g); Vb is the volume of sodium hydroxide used for blank sample (mL); Va is the volume of sodium hydroxide used for the sample (mL); M is the molar concentration of sodium hydroxide (mol/L); t is the time reaction (min); m or v is the mass (mg) or volume (mL), respectively, of enzyme.

2.7 Biochemical Properties: pH and temperature influence

For determining the influence of pH and temperature over the enzyme, the previous methodology was used, varying the sodium phosphate buffer pH (4.0, 5.0, 6.0, 7.0, 8.0, 9.0) and preserving the temperature at 37 °C (pH influence), or varying the temperature of water bath (40, 45, 50, 55, 60 °C) and preserving the buffer pH in 7.0 (temperature influence).

The optimum pH and temperature of the lipases used in this work according to the manufacturer were: AKL (pH 8.0, 55 °C); PCL (pH 8.0, 37 °C); HPL (pH 7.5, 40 °C); PPL (pH 7.5, 40 °C); MJL (pH 8.0, 50 °C).

2.8 Biochemical Properties: substrate concentration influence

The influence of initial concentration of substrate over the reaction rate, and the occurrence of some type of enzyme inhibition were studied according to previous methodology of hydrolytic activity using AKL, and varying the olive oil proportion on substrate (5 to 50% (v/v)). The assays were carried out at 37 °C and pH 7.0, and k_m and V_{max} values were calculated using Line weaver-Burk equation.

2.9 Thermal Stability

The thermal stability of immobilized enzyme was evaluated by incubation of samples (100 mg) at 40, 50, and 60 °C in aqueous solution of sodium phosphate buffer (0.1 mol/L, pH 7.0) for 60 min. After thermal treatment, the samples were immediately cooled in ice bath in order to stop the enzymatic inactivation reaction, and the residual activity was measured. The inactivation constant (k_d) for immobilized lipase was calculated by Eq. (3), where A_{in} is the residual activity after thermal treatment (U/g), A_{in0} is the residual activity before thermal treatment (U/g), and t is the time of incubation (h).

$$ln\left(\frac{A_{in}}{A_{ino}}\right) = K_d * t \tag{3}$$

The half-life time ($t_{1/2}$ (h)) was obtained according to Eq. (4).

$$t_{1/2} = \frac{0{,}693}{K_d} \tag{4}$$

2.10 Esterification Activity

Firstly, the hexane was treated to decrease water percentage in order to avoid any interference in esters formation. A 500 ml volume of hexane was treated with 4 g of magnesium sulfate and left to rest at room temperature for 2 hours in order to decrease water percentage and avoid any interference in esters formation [25]. The esterification activity of immobilized lipase was determined through the reaction, at equimolar ratio, of isoamyl alcohol (0.06 mol/L) with acetic acid (0.06 mol/L) in hexane, producing the aromatic ester isoamyl acetate. The reactions were carried out in a 100 mL-closed flasks at 40 °C by adding 0.250 g of dry weight enzyme (free and immobilized) to 40 mL of reaction media in rotational shaker at 200 rpm. A blank reaction was also conducted in order to evaluate the spontaneous formation of esters. Aliquots of 1 mL were removed from the reaction after 6, 12, 24, 36, 42, 48, 54, 68, 80, and 92 hours, and the amount of esters produced was quantified by titration. One unit of esterification activity was defined as the amount of enzyme necessary for formation of 1 µmol of ester per minute of reaction at assay conditions [25].

2.11 Residual Acid Determination

The residual acid concentration was determined by titration of aliquots dissolved in 15 mL of acetone-ethanol solution 1:2 with 0.02 mol/L sodium hydroxide and 1% phenolphthalein as indicator. The math was done by equation (5), where C is the percentage of acid (%), V is the volume of sodium hydroxide used (mL), N is the concentration of sodium hydroxide (mol/L), M is the molar weight of acid (g/mol), and W is the weight that corresponds to 1 mL of aliquot used for titration.

$$C = \frac{V * N * M}{10 * W} \tag{5}$$

The esterification percentage corresponds to the consumed acid percentage, according to Eq. (6), where C_i is the initial concentration of free residual acid (mol/L), and C is the concentration of free residual acid at a time (mol/L).

$$\%\, esterification = \frac{(C_i - C)}{C_i} * 100 \tag{6}$$

III. RESULTS AND DISCUSSION

3.1 Hydrolytic Activity of free lipases

In a first step, the selection of commercial lipases that presented potential and satisfactory results for immobilization was performed. Table 1 presents the preliminary results obtained in this first stage of selection of commercial lipases.

TABLE 1
HYDROLYTIC ACTIVITY OF COMMERCIAL LIPASES

Lipase	Hydrolytic Activity (U/g)
AKL	3323.6
PSL	2646
PHL	1839.6
PPL	868
MJL	725.2

From the results presented in Table 1, the best ones were obtained from *Pseudomonas fluorences* (AKL) and *Pseudomonas cepacia* (PSL) lipases, with hydrolytic activity of 3323.6 U/g and 2646 U/g, respectively. Then, the enzymes AKL and PSL were selected to proceed with immobilization processes.

3.2 Initial protein load and immobilization protocol selection

Both previously selected lipases were immobilized in PHB and chitosan by physical adsorption and entrapment with initial protein load of 5 and 10 mg/g. Table 2 shows the results obtained for physical adsorption.

The immobilization of lipase by physical adsorption proved to be efficient, providing a significant increase in almost all protocols used, which implies that the active site of the enzymes was not blocked. The highest activity for immobilization by physical adsorption was obtained for AKL in PHB with 5 mg/g of initial protein loading (698.60 ± 5.53 U/g), with immobilization yield of 87.30 ± 1.909 %.

By evaluating the performance of the supports used, PHB presented higher final hydrolytic activities for both enzymes and initial protein loading compared to the results from chitosan. This one was more efficient in terms of hydrolytic activity in PSL immobilization only, resulting in 510.46 ± 0.46 U/g and 99.63 ± 0.454 % of immobilization yield for PSL with 10 mg/g of initial protein loading.

TABLE 2
HYDROLYTIC ACTIVITY OF IMMOBILIZED ENZYME; INITIAL AND FINAL PROTEIN CONCENTRATION; YIELD OF IMMOBILIZATION, AND IMMOBILIZED PROTEIN FOR PHYSICAL ADSORPTION PROTOCOL

Lipase IPL* + Support	Immobilized Enzyme Activity (U/g)	Initial Protein (mg/g)	Final protein (mg/g)	IY (%)
AKL 5 mg/g + Chit	289.59 ± 0.46	0.303 ± 0.007	0.293 ± 0.008	96.57 ± 0.493
AKL 10 mg/g + Chit	61.83 ± 0.45	0.163 ± 0.008	0.132 ± 0.011	80.63 ± 0.382
AKL 5 mg/g + PHB	698.60 ± 5.53	0.300 ± 0.0124	0.262 ± 0.005	87.30 ± 1.909
AKL 10 mg/g + PHB	683.57 ± 5.48	0.140 ± 0.0109	0.1287 ± 0.002	92.10 ± 5.644
PSL 5 mg/g + Chit	406.37 ± 0.44	0.0389 ± 0.0005	0.0372 ± 0.015	95.95 ± 5.155
PSL 10 mg/g + Chit	510.46 ± 0.46	0.0238 ± 0.0087	0.0237 ± 0.009	99.63 ± 0.454
PSL 5 mg/g + PHB	677.09 ± 5.70	0.0419 ± 0.0096	0.0393 ± 0.013	92.44 ± 10.107
PSL 10 mg/g + PHB	672.61 ± 5.28	0.029 ± 0.0056	0.0284 ± 0.005	98.20 ± 1.507

IPL: initial protein load

Analyzing the influence of the initial protein loading, it can be inferred that the increase from 5 to 10 mg/g did not affect the immobilization of PSL, whereas the immobilization of AKL seemed to have been affected when using chitosan as support, decreasing from 289.59 U/g to 61.83 U/g. The size of enzymes and pores of supports may have influence on that result.

Dabaja et al. [26] utilized PHB as immobilization support, and the same initial protein loading as the present work. They were able to achieve 291.03 U/g for 5 mg/g of initial protein loading, which shows the potential of the present work that, with the same conditions, obtained 698.60 U/g.

The protocol of immobilization was chosen according to the highest hydrolytic activity obtained, which turned out to be AKL, 5mg/g in PHB, with 698.60 ± 5.53 U/g for physical adsorption. The second immobilization method evaluated was sodium alginate encapsulation. AKL and PSL lipases with initial concentration of 5 and 10 mg/mL, and different $CaCl_2$ concentrations (0.1 and 0.2 mol/L) were tested for alginate bead formation. The results are presented in Table 3.

TABLE 3
HYDROLYTIC ACTIVITY OF IMMOBILIZED ENZYME; INITIAL AND FINAL PROTEIN CONCENTRATION; YIELD OF IMMOBILIZATION, AND IMMOBILIZED PROTEIN FOR ENTRAPMENT PROTOCOL.

Lipase IPL* + [$CaCl_2$]	Immobilized Enzyme Activity (U/g)	InitialProtein (mg/g)	Final protein (mg/g)	IY (%)
PSL 5 mg/g + 0.1 mol/L	102.67 ± 0.69	0.857 ± 0.004	0.822 ± 0.0025	95.85 ± 0.173
PSL 5 mg/g + 0.2 mol/L	81.35 ± 1.17	0.844 ± 0.007	0.819 ± 0.0107	96.91 ± 2.128
PSL 10 mg/g + 0.1 mol/L	182.46 ± 1.80	0.867 ± 0.0005	0.807 ± 0.0008	93.09 ± 0.042
PSL 10 mg/g + 0.2 mol/L	111.14 ± 1.32	0.857 ± 0.0016	0.815 ± 0.0008	95.10 ± 0.087
AKL 5 mg/g + 0.1 mol/L	247.30 ± 1.13	0.920 ± 0.0016	0.817 ± 0.0041	88.82 ± 0.609
AKL 5 mg/g + 0.2 mol/L	144.92 ± 1.43	0.897 ± 0.0207	0.816 ± 0.0041	90.97 ± 1.261
AKL 10 mg/g + 0.1 mol/L	176.51 ± 1.63	0.883 ± 0.0058	0.816 ± 0.0058	92.40 ± 1.261
AKL 10 mg/g + 0.2 mol/L	152.93 ± 1.18	0.882 ± 0.0016	0.807 ± 0.0058	91.52 ± 0.485

IPL: initial protein load

From the results presented in Table 3, the encapsulation immobilization protocol was efficient in increasing the hydrolytic activity of the enzymes in all tested protocols. However, when compared to the results of physical adsorption, the encapsulation was less efficient in preserving the hydrolytic properties. The decrease in HA may have been caused by diffusional limitations faced by the pores formation in the alginate spheres, reducing the formation of enzyme-substrate complex and hence the product formation.

The catalytic properties of immobilized enzymes can be influenced by three forms of interaction: the binding of the enzyme in the matrix may cause conformational changes that affect the tridimensional structure of the enzyme; substrate access to the active site may be affected by steric hindrance of the support; and the support properties can affect the mode of action of the enzyme [27]. The influence of initial protein loading resulted in an increase of HA with the increase in initial protein provided, except for the combination of AKL immobilized in 0.1 mol/L sodium alginate. The concentration of sodium alginate, in turn, had a negative influence on HA, which implies that the increase in sodium alginate concentration resulted in spheres with smaller pore diameters, so a steric hindrance occurs and the substrate does not reach the active site of enzyme properly.

Teixeira et al. [28] used calcium alginate and the same initial protein loading in their study, and they obtained lower HA for the immobilized enzymes than these work shows, which confirms the efficiency of sodium alginate in entrapment immobilization.

Lipase immobilization by entrapment had its best result when using AKL 5 mg/mL, 0.1 mol/L $CaCl_2$, with 247.30 ± 1.13 U/gof HA.

In order to proceed with the work, the best result from physical adsorption and entrapment immobilization were used to study the influence of pH, temperature, substrate concentration, thermal stability, and ester synthesis.

3.3 Influence of pH

The medium pH can influence the structure of enzymes, and, consequently, their activity, in a manner that the enzyme presents an optimal pH value. Immobilized enzymes may follow the typical behavior of free enzymes, but the pH profile of immobilized and free enzymes is not always the same, as the immobilization process may induce conformational changes [15]. The results for physical adsorption and entrapment are shown in Fig. 1.

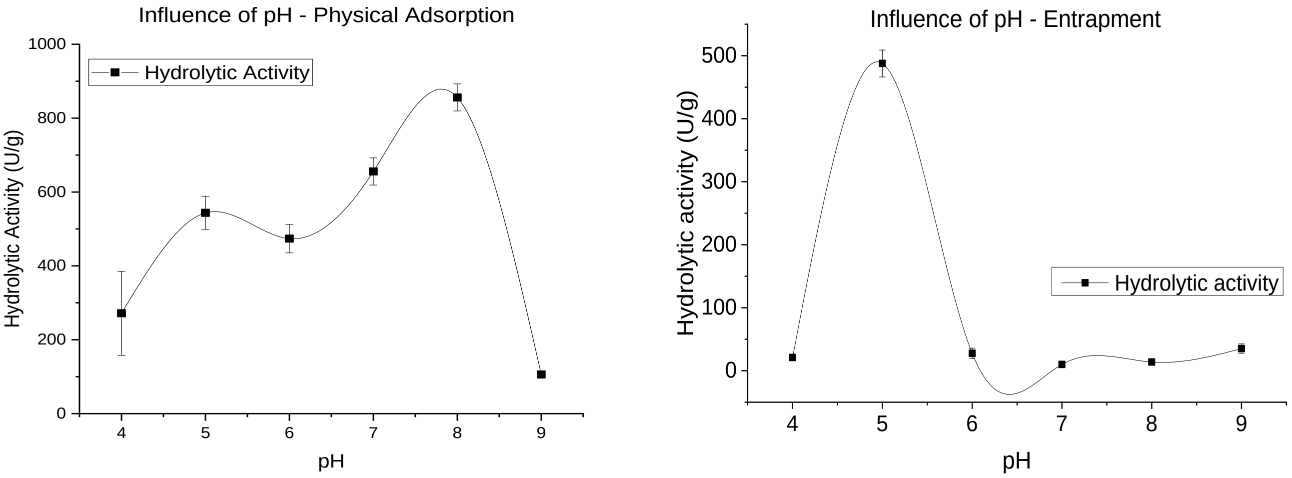

FIGURE 1: Influence of pH on immobilization of AKL by physical adsorption (a) and entrapment (b)

For physical adsorption (Fig. 1a), the optimum pH was 8.0 (856.10 ± 36.65 U/g), which is the same as presented by the manufacturer for free lipase. Below or above this pH value, there are changes in enzyme 3D structure that harm its activity.

For entrapment (Fig. 1b), the immobilized enzyme presented an optimal pH of 5, with HA of 487.69 ± 21.36 U/g. In this case, a shift from 8 to 5 of optimum pH is observed upon immobilization.

Optimum pH of 8.0 was also obtained by Dabaja et al. [26] and Tintor et al. [29].

3.4 Influence of Temperature

The rate of enzymatic reactions is extremely temperature dependent. Increasing the temperature gives rise to the energy of the molecules and thereby increases the enzymatic activity. However, at very high temperatures, the enzyme may be denatured and thus lose its activity [15]. Fig. 2 presents the influence of temperature on immobilization of AKL by physical adsorption (Fig. 2a) and entrapment (Fig. 2b).

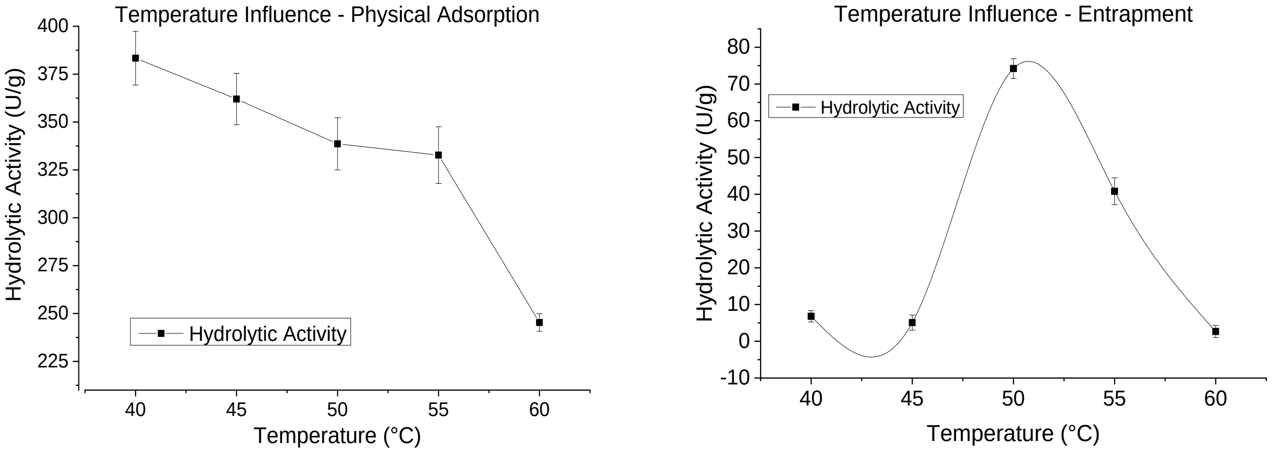

FIGURE 2: Influence of temperature on immobilization of AKL by physical adsorption (a) and entrapment (b).

From Fig. 2a, it was found that the best temperature for immobilized AKL by physical adsorption was 40 °C, with 383.37 ± 13.76 U/g, which is lower that the optimum temperature presented by the manufacturer for free lipase (55 °C). For some industrial processes, the products are heat sensible, so the decrease in optimum temperature becomes an advantage for those applications. For immobilization by entrapment, Fig. 2b shows that there was not a great shift of optimum temperature, since the immobilized lipase showed its higher activity at 50°C. Nevertheless, unlike the physical adsorption, the hydrolytic activity decreased considerably at higher temperatures, suggesting a poor thermal stability.

3.5 Influence of substrate concentration

The analysis of kinetic parameters such as K_m and V_{max} is important because they reveal the specificity changes in relation to the substrates that the enzymes undergo after immobilization process [30]. Fig. 3 presents the influence of substrate concentration (olive oil) on reaction rate using immobilized AKL by physical adsorption (Fig. 3a) and entrapment (Fig. 3b).

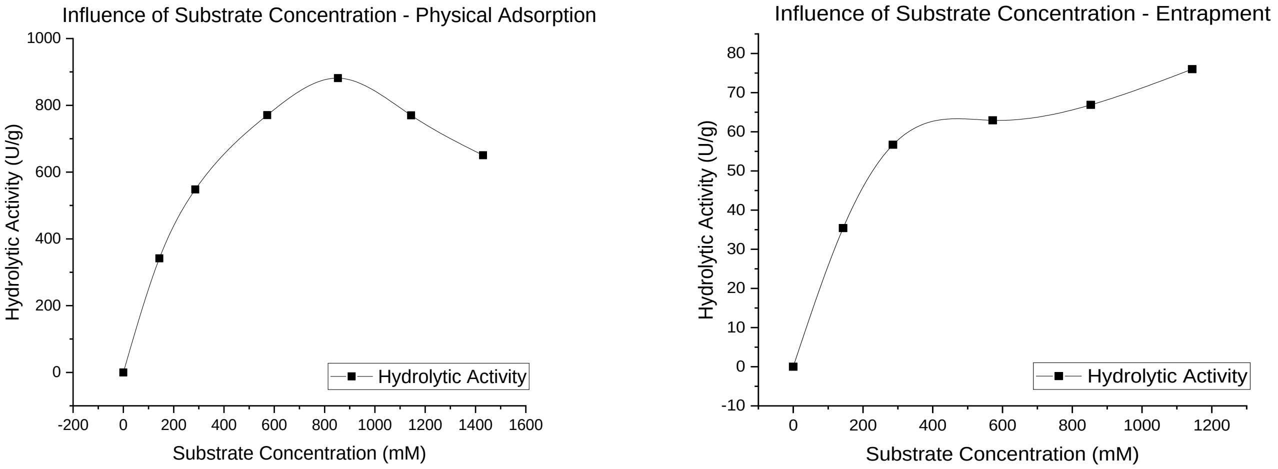

FIGURE 3: Influence of substrate concentration (olive oil) on reaction rate using immobilized AKL by physical adsorption (a) and entrapment (b).

Analyzing the results from Fig. 3a, it can be noted that for the physical adsorption procedure, he ratio that presented the highest activity was 30 % of olive oil and 70% of water, with an activity of 881.30 U/g and the profile obtained follows the Michaelis-Menten model. For immobilization by entrapment (Fig. 3b), the best substrate concentration was 40%, with activity of 75.99U/g, and it also followed the Michaelis-Menten model profile.

From the obtained data, it was possible to use Lineweaver-Burk linearization tool in a graph of 1/HA versus 1/S, where HA is the hydrolytic activity, and S is the substrate concentration in order to calculate the affinity constant (K_m) and the maximum reaction rate (V_{max}). For the adsorption protocol, K_m and V_{max} were 0.05 mM and 1000 µmol/min.g, respectively, and for the entrapment protocol K_m was 0.03 mM, and V_{max} was 81.97 µmol/min.g.

AKL immobilized by physical adsorption in PHB showed an apparent V_{max} value of 1000 U/g and K_m of 0.05 mM, while when immobilized by entrapment in sodium alginate, it presented much lower V_{max} (81.97 U/g), and similar, but lower K_m (0.03 mM), which confirms the diffusional problems presented by the entrapment method, since the reaction catalyzed by AKL in PHB is much faster than the reaction catalyzed by AKL in alginate.

3.6 Thermal stability

The results for thermal stability for both immobilization methods are presented in Table 4.

TABLE 4
RESIDUAL ACTIVITY OF IMMOBILIZED LIPASE WITHIN AFTER 60 min-incubation.

PhysicalAdsorption		**Entrapment**	
Temperature(°C)	**Residual Activity (U/g)**	**Temperature(°C)**	**Residual Activity (U/g)**
40	610.44 ± 25.64	40	74.92 ± 16.26
50	613.63 ± 78.02	50	172.36 ± 12.47
60	655.69 ± 6.59	60	221.36 ± 44.17

It can be observed that for all temperatures applied, AKL immobilized in both methods presented good thermal stability since it did not lose activity with the increase in incubation temperature, avoiding enzyme denaturation and damage to the structure of sodium alginate beads. From the data presented in Table 4, it was possible to calculate de inactivation constant (k_d) and the half-time life ($t_{1/2}$) for immobilized lipases, and the results are shown in Table 5.

TABLE 5
INACTIVATION CONSTANT AND HALF-LIFE TIME FOR IMMOBILIZED LIPASE.

	Physical Adsorption		**Entrapment**	
Temperature (°C)	**K_d (h^{-1})**	**$t_{1/2}$ (h)**	**K_d(h^{-1})**	**$t_{1/2}$ (h)**
40	0.1349	5.137	1.1942	0.5803
50	0.1297	5.344	0.3610	1.9195
60	0.0634	10.931	0.1108	6.2540

For the immobilization by physical adsorption, the temperature of 60 °C presented the longest half-time life (10.931 h), and for immobilization by entrapment, the longer time was 6.2540 h, which means that the enzyme immobilized by physical adsorption lasts more time to reduce its activity to 50 % of the initial value.

For both immobilizations methods, it was observed that the half-life time increased with the increment in temperature. From the results obtained in Table 5, indicate that for both immobilization methods, the enzyme immobilized derivative can be used at higher temperatures, without significant loss of its activity and such result is of great importance for future industrial application.

3.7 Application: Esterification reaction (Synthesis of esters and flavorings)

The synthesis of esters via enzymatic route involves a complex mechanism dependent on the type of substrate, enzyme, organic solvent, and concentration of the reaction medium. The aromatic ester selected was isoamyl acetate, characterized by the aroma of banana and pear.

A comparison of the performance of free and immobilized lipases was carried out alongside a control (a reaction without the presence of enzyme). Acid consumption and ester formation were quantified by titration method through the disappearance of fatty acid. The residual acid content was calculated from Eq. 6 and the results are shown in Table 6.

TABLE 6
ISOAMYL ACETATE YIELD PERCENTAGE WITHIN 78 H OF REACTION.

Time(h)	Adsorption	Entrapment	Free lipase
6	31.187	28.147	17.146
12	29.686	29.745	26.204
24	23.951	19.112	34.403
36	31.338	26.459	35.008
48	41.456	30.179	34.977
54	9.558	32.850	54.147
60	74.264	26.989	36.823
66	16.898	32.048	50.400
72	34.425	37.843	40.052
78	7.079	41.992	40.033

From Table 6, the formation of isoamyl acetate was higher when using immobilized lipase by physical adsorption, with 74.264% after 60 h of reaction, whereas immobilized lipase by entrapment achieved 41.992% after 78 h, and free lipase achieved 54.15% after 54 h. Although the immobilized lipase by physical adsorption presented a better esterification yield, its profile was not linear, increasing exponentially within 54 h of reaction and remaining below 50% after 60 h of reaction. On the other hand, the immobilized lipase by entrapment kept a linear profile, achieving the maximum percentage yield after 78 h of reaction.

IV. CONCLUSION

At the end of this work it is possible to consider that both immobilization methods presented satisfactory results as the enzymes were able to increase their hydrolytic activity under several conditions. The lipase immobilized by physical adsorption demonstrates the potential of PHB *in natura* to be used as support for lipase immobilization. Free and immobilized lipases had similar operating conditions, and the the PHB immobilized AKL showed the best percentage yield of isoamyl acetate formation after 60h-reaction (74.26%).

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Kinetics of Initiated Ethanediol Formation from Methanol–Formaldehyde Solutions

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Abstract — The mechanism and kinetics are developed for the initiated non branched-chain formation of ethanediol in methanol–formaldehyde solutions at formaldehyde concentrations of 0.1–3.1 mol dm^{-3} and temperatures of 373–473 K. The experimental concentrations of the free insolated form of formaldehyde are given at the different temperatures and total concentrations of formaldehyde in methanol. The experimental dependence of the radiation-chemical yields of ethanediol on formaldehyde concentration in γ-radiolysis of methanol–formaldehyde solutions at 373–473 K is shown. At a formaldehyde concentration of 1.4 mol dm^{-3} and T = 473 K, the radiation-chemical yield of ethanediol is 139 molecules per 100 eV. The effective activation energy of ethanediol formation is 25 ± 3 kJ mol^{-1}. The quasi-steady-state treatment of the reaction network suggested here led to a rate equation accounting for the non monotonic dependence of the ethanediol formation rate on the concentration of the free (unsolvated) form of dissolved formaldehyde. It is demonstrated that the peak in this dependence is due to the competition between methanol and CH_2=O for reacting with the adduct radical $HOCH_2CH_2O^{\bullet}$.

Keywords* — *Methanol, Formaldehyde, Formation, Ethanediol, Radiation-Chemical Yield, Rate Equation.

I. INTRODUCTION

Ethanediol is widely used in the production of polyester fibers and films, antifreezes, hydraulic and quench liquids, alkyds, polyurethanes, etc. The main commercial method of ethanediol synthesis is ethylene oxide hydration. The annual world ethanediol output is over 20 million tons.

These facts stimulate development of new, energetically efficient ethanediol synthesis technologies. A possible one is radiation-chemical synthesis using a dual-purpose heterogeneous nuclear reactor in which the graphite moderator is replaced with a methanol–formaldehyde mixture and the heat carrier is steam flowing past fuel elements. A technological analysis of this system demonstrated that, at a reactor thermal power of 2.5 GW, it is possible to profitably manufacture 80 thousand tons of ethanediol per year along with producing 677 MW electric powers.

Here, we report the experimental dependences of the radiation-chemical yield of ethanediol on the total formaldehyde concentration at different temperatures and present the reaction network deduced for the process examined. By applying quasi-steady-state treatment to this network, we obtain a rate equation for ethanediol formation.

II. EXPERIMENTAL

The experimental procedure used in this study, including the gas chromatographic analysis of stable products, was described in our earlier publication [1]. The concentration x of the free formaldehyde species in a methanol solution was determined by high-temperature UV spectrophotometry in the range 375–391 K at the total formaldehyde concentration c_0 (free and bound species including the concentration of polymer solvates) of 1.0–7.0 mol dm^{-3}. The ^{60}Co γ-radiation dose rate was 6.9 Gy s^{-1}, as determined with a ferrous sulfate dosimeter. The dose absorbed by the solution with the electron density of methanol taken into account was (1.25–6.28) ×10^4 Gy. The total relative error of the experiment was ≤ 10 %.

The rate equations were derived by quasi-steady-state treatment, which is most suitable for describing the processes including at least eight to ten reactions with four to six different free radicals and at most three to seven experimental points in their functional curves, using the condition for the rest steps of the process that makes it possible to reduce the exponent of term $2k_5[^{\bullet}CH_2OH]^2$ to 1 in equation $d[^{\bullet}CH_2OH]/dt = 0$: $k_6 = \sqrt{2k_5 2k_7}$ and $V_1 = V_5 + 2V_6 + V_7 = (2k_5[^{\bullet}CH_2OH] + 2k_7[^{\bullet}CHO])^2$ [2].

III. RESULTS AND DISCUSSION

The effect of temperature on the yields of the ultimate products of the γ-radiolysis of formaldehyde solutions in saturated aliphatic alcohols was considered elsewhere [1]. 1-Hydroxyalkyl radicals add to the carbon atom at the double bond of the carbonyl group of the free (unsolvated, monomeric) form of formaldehyde dissolved in the saturated alcohol [3]. At room temperature, the concentration of this form in the solution is a fraction of a percent of the total formaldehyde concentration (which includes the formaldehyde chemically bonded with the solvent), and it increases exponentially as the temperature is raised [4]. The solvent concentration in formaldehyde solutions at a given temperature can be estimated by the method suggested by Silaev [5].

Figure 1 shows the Arrhenius plot of the ethanediol yield for the γ-radiolysis of 0.9 mol dm^{-3} solutions of formaldehyde in methanol [1]. As the temperature is elevated from 373 to 473 K, the free formaldehyde concentration calculated from earlier data [4] increases from 2.78 ×10^{-3} to 0.16 mol dm^{-3}. The effective activation energy of ethanediol formation is 25 ± 3 kJ mol^{-1}.

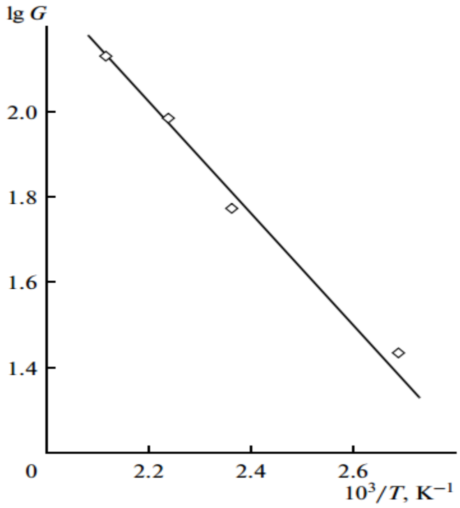

FIGURE 1: Logarithm of the ethylene glycol yield *G* (molecule/100 eV) versus inverse temperature for the γ-radiolysis of the methanol–formaldehyde (0.9 mol dm^{-3}) system [1].

Figure 2 plots the ethanediol yield as a function of the total concentration of formaldehyde (0.1, 0.3, 0.6, 0.9, 1.4, 2.2, and 3.1 mol dm^{-3}), including its free and alcohol-bound forms [3], in the methanol–formaldehyde system at 373, 423, 448, and 473 K [6]. The maximum product yield is 139 molecules per 100 eV (144 mol × 10^{-7} J) at a formaldehyde concentration of 1.4 mol dm^{-3} at 473 K. There is no maximum in the product yield versus concentration curve at 373 K up to the highest formaldehyde concentration examined, 3.1 mol dm^{-3}. At higher temperatures, the curves have a maximum at a formaldehyde concentration of about 1.4 mol dm^{-3}. The maximum in these curves arises from the competition between methanol and free formaldehyde (CH_2=O) for reacting with the adduct radical $HOCH_2CH_2O^•$.

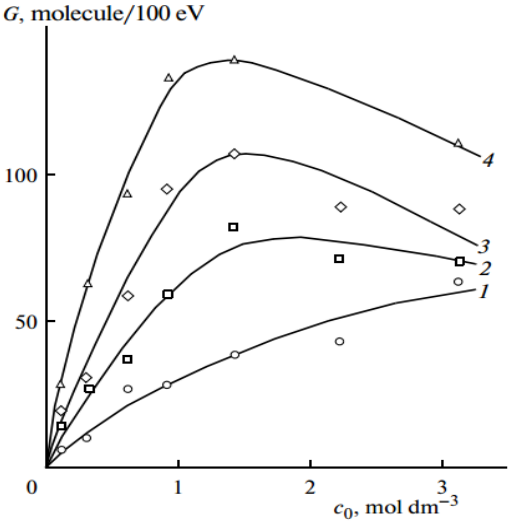

FIGURE 2: Ethylene glycol yield *G* as a function of the total form aldehyde concentration c_0 for the γ-radiolysis of the methanol–formaldehyde system at *T* = 373 (*1*), 423 (*2*), 448 (*3*), and 473 (*4*) K [6].

The main by-product of γ-radiolysis in the methanol–formaldehyde system is methylal, $CH_2(OCH_3)_2$, which results from the thermal acetalization of formaldehyde. The second most abundant by-product is methyl format, CH_3OCHO, which also results from the thermal reversible conversion of formaldehyde [3, 7]. The concentrations of these products in the solution irradiated to a dose of 7.56×10^4 Gy at 473 K are, respectively, 0.56 and 0.08 mol dm^{-3}, which are 23.3 and 3.3% of the total initial formaldehyde concentration in the system (2.4 mol dm^{-3}).

The kinetics of the initiated non branched-chain addition of 1-hydroxyalkyl radicals to free (unsolvated) formaldehyde $CH_2{=}O$ in the γ-radiolysis of saturated aliphatic alcohol–formaldehyde systems, which yields vicinal glycols, carbonyl compounds, and methanol via a chain mechanism, was considered in earlier works [2, 8].

The data available on the methanol–formaldehyde system can be accounted for in terms of the following reaction network.

Chain initiation

$$1.\ CH_3OH \xrightarrow[-H^\bullet]{} {}^\bullet CH_2OH.$$

Chain propagation

$$2.\ {}^\bullet CH_2OH + CH_2O \xrightarrow{k_2} HOCH_2CH_2O^\bullet,$$

$$3.\ HOCH_2CH_2O^\bullet + CH_3OH \xrightarrow{k_3} HOCH_2CH_2OH + {}^\bullet CH_2OH,$$

$$3a.\ HOCH_2CH_2O^\bullet \xrightarrow{k_{3a}} CH_2O + {}^\bullet CH_2OH.$$

Inhibition

$$4.\ HOCH_2CH_2O^\bullet + CH_2O \xrightarrow{k_4} HOCH_2CH_2OH + {}^\bullet CHO.$$

Chain termination

$$5.\ 2{}^\bullet CH_2OH \xrightarrow{2k_5} HOCH_2CH_2OH$$

$$(\text{or: } CH_3OH + CH_2O;\ OHCCHO + 2H_2;\ 2CH_2O + H_2),$$

$$6.\ {}^\bullet CH_2OH + {}^\bullet CHO \xrightarrow{k_6} HOCH_2CHO$$

$$(\text{or: } 2CH_2O;\ CH_3OH + CO;\ OHCCHO + H_2),$$

$$7.\ 2{}^\bullet CHO \xrightarrow{2k_7} OHCCHO$$

$$(\text{or: } CH_2O + CO;\ 2CO + H_2).$$

In these reactions, ${}^\bullet CH_2OH$ is the reactive hydroxymethyl radical (addend), $HOCH_2CH_2O^\bullet$ is the reactive hydroxyethoxyl radical (adduct), ${}^\bullet CHO$ is the low-reactive formal radical (inhibitor), $HOCH_2CH_2OH$ is ethanediol, $HOCH_2CHO$ is glycolaldehyde, and OHCCHO glycol is glyoxal. Of the above molecular products, only ethanediol forms *via* a chain mechanism. Reaction 1 can be initiated by a peroxide [9], light [10], or γ-radiation [6].

The chain propagation and inhibition steps of reaction network include the pairs of consecutive reactions 2–3 and 2–3a; the pairs of parallel (competing) reactions 3–3a, 3–4, and 3a–4; and consecutive–parallel reactions 2 and 4. Reaction 3a is the reverse of reaction 2.

Reaction 5 yields an additional amount of ethanediol through the dimerization of the hydroxymethyl chain carrier radical. The disproportionation of this radical can be neglected [11].

The possible abstraction reaction

2a. $^{\bullet}CH_2OH + CH_2O \xrightarrow{k_{2a}} CH_3OH + {}^{\bullet}CHO$,

which is parallel to addition reaction 2, is not included in the reaction network for the reason that it does not regenerate the addend radical $^{\bullet}CH_2OH$. Besides, it is in essential for the kinetic description of the process because the rate ratio of these reactions, $V_2/V_{2a} = k_2/k_{2a}$, is independent of the concentration of the unsaturated component ($CH_2{=}O$) in the system. The addition of the adduct radical $HOCH_2CH_2O^{\bullet}$ to formaldehyde at elevated temperatures seems unlikely because it would yield an ether linkage.

The hydroxyethoxyl adduct radical $HOCH_2CH_2O^{\bullet}$ resulting from reaction 2 must possess an increased energy due to the energy released upon the conversion of the double bond C=O into an ordinary bond (30–60 kJ mol^{-1} for the addition of C_1–C_4 alkyl radicals to formaldehyde in the gas phase under standard conditions[12, 13]). Therefore, this radical is able both to abstract a hydrogen atom from the nearest methanol and formaldehyde molecules via reactions 3 and 4, respectively, and to decompose via a monomolecular mechanism including isomerization [2, 8] (reaction 3a) just on the spot, with-out diffusing in the solution and, accordingly, without participating in radical-radical termination reactions 5–7. A specific feature of the ethanediol buildup kinetics is that the decomposition reaction 3a of the adduct radical (whose probability increases with increasing temperature [8]) in the methanol–formaldehyde system is the reverse of the formation reaction 2 of this adduct radical.

The formyl radical $^{\bullet}CHO$ resulting from reaction 4, which is in competition with reactions 3 and 3a, is comparatively low-reactive because of the possibility of the partial delocalization of its spin density from the carbon atom via the double bond to oxygen, an element with a higher electron affinity [14]. For example, unlike the methyl and alkoxyl π-radicals, the formyl σ-radical can be stabilized in glassy alcohols at 77 K [15]. The stabilization energy of the formyl radical in the standard state in the gas phase is –24.3 kJ mol^{-1}[16]. In the gas phase, the C–H bond dissociation energy for the formyl radical is half the same energy for the acetyl radical and is almost 5 times lower than the Cα–H bond dissociation energy for the saturated C_1–C_3 alcohols [14]. As distinct from reactions 3 and 3a, reaction 4 wastes $HOCH_2CH_2O^{\bullet}$ adduct radicals without regenerating the chain-carrier addend radical $^{\bullet}CH_2OH$, causing the termination of the kinetic chain through the formation of the low-reactive radical $^{\bullet}CHO$. Along with the $^{\bullet}CH_2OH + {}^{\bullet}CHO$ combination reaction 6, reaction 4 inhibits the nonbranched-chain process.

The following rate equation was set up by quasi-steady-state treatment for ethanediol formation via the chain mechanism (reaction 3) and the non chain mechanism (reactions 4 and 5) [8]:

$$V_{3,4,5}(CH_2OH)_2 = V_1[f(\alpha l + x)k_2 x + V_1 2k_5(\alpha l + \beta + x)^2]f^{-2} \tag{1}$$

where $f = k_2x^2 + (\alpha l + \beta + x)\sqrt{2k_5V_1}$; V_1 is the initiation rate, mol dm^{-3} s^{-1}; l –concentration (mol dm^{-3}) of methanol at a given concentration of formaldehyde dissolved in it, x –concentration (mol dm^{-3}) of free (unsolvated) formaldehyde, at that $l = [CH_3OH] >> [CH_2{=}O] = x$; $\alpha = k_3/k_4$ and $\beta = k_{3a}/k_4$ – ratios of the rate constants (dm^3 mol^{-1} s^{-1}) of the competing (parallel) reactions, the latter in units of mol dm^{-3}.

The experimental concentrations x of free (unsolvated) formaldehyde at different temperatures and total formaldehyde concentrations c_0, measured at room temperature, in methanol are given in the Table 1. The free formaldehyde concentration x increases with the temperature according to an exponential law [4] and decreases with the solvent permittivity at a constant temperature [17].

The following empirical equation relating the concentration x (mol dm^{-3}) of free formaldehyde to temperature T (K) and the total concentration c_0 in the solution (measured at room temperature), was developed by the treatment of 101 data points [4]:

$$\lg x = -a\,(10^3/T) + b + h \lg c_0, \tag{2}$$

where the coefficients a and b were calculated as the parameters of a straight-line equation by the least-squares technique from the dependence of lg x on $1/T$ at c_0 = 1.0 mol dm^{-3} for various solvents, and the coefficient h was obtained as the average value of the slopes of lg x as linear functions of lg c_0 at various series of fixed temperatures. For methanol–formaldehyde solutions, the coefficients a = 3.11, b =5.58, and $h = 0.22\ c_0 / \lg c_0$, the calculated concentrations x_{calc} of free formaldehyde are given in the Table 1.

TABLE 1:
EXPERIMENTAL x AND CALCULATED x_{calc} CONCENTRATIONS (mol dm^{-3}) OF FREE (UNSOLVATED) FORMALDEHYDE AT DIFFERENT TEMPERATURES T (K) AND TOTAL FORMALDEHYDE CONCENTRATIONS c_0 (mol dm^{-3}), MEASURED AT ROOM TEMPERATURE, IN METHANOL [4]

c_0	T	$10^2 x$	$10^2 x_{calc}$
1.0	375	0.33	0.32
1.0	395	1.00	0.84
1.0	423	2.90	2.80
2.5	373	0.60	0.62
2.5	385	1.15	1.13
2.5	398	1.80	2.07
5.4	351	0.78	0.81
5.4	383	3.70	4.45
5.4	398	6.80	8.99
7.0	365	4.70	3.98
7.0	383	12.50	10.0
7.0	391	16.00	14.7

Note that Eq. (1) presented in a previous work [2] does not take into account reaction 3a. The rate ratios of the competing reactions are $V_3/V_4 = \alpha l/x$ and $V_{3a}/V_4 = \beta/x$, and the chain length is $\nu = (V_3 + V_{3a})/V_1$.

Equation (1) can be put into a simpler form [8] by ignoring the ethanediol yield from the dimerization reaction 5, which is insignificant as compared to the total ethanediol yield from reactions 3 and 4:

$$V_{3,4}(CH_2OH)_2 = \frac{V_1(\alpha l + x)k_2 x}{k_2 x^2 + (\alpha l + \beta + x)\sqrt{2k_5V_1}}, \tag{3}$$

Dividing the numerator and denominator of Eq. (3) by $k_{-2} \equiv k_{3a}$ makes it possible to replace k_2 with $K_2 = k_2/k_{-2}$, the equilibrium constant of reversible reaction 2. Leaving aside the reverse of reaction 2 reaction 3a ($k_{3a} = 0, \beta = 0$) will further simplify Eq. (3). In this case, the rate constant k_2 will be an effective quantity.

Equation (1) when $k_2x^2 << (\alpha l + \beta + x)\sqrt{2k_5V_1}$ (ascending branch of the curve having a maximum) and $\alpha l >> \beta$ (practically without reaction 3a) is transformed to a simple directly-proportional dependence on the concentration x of free formaldehyde, which can be used to pre-estimate the parameter k_2:

$$V_{3,4,5} = (V_1/\varphi^2)[(\varphi\, k_2 x/\sqrt{2k_5V_1}) + 1] \tag{4}$$

were $\varphi = 1$ for the ascending portion of the curve and $\varphi = 2$ for the maximum, when $k_2x^2 \cong (\alpha l + \beta + x)\sqrt{2k_5V_1}$.

Examples of fitting the experimental dependences of the vicinal glycol formation rate V (or radiation-chemical yield G) on the free formaldehyde concentration x in alcohol–formaldehyde systems to Eq. (2) are presented in earlier publications [2, 8].

The relationships between the reaction rates V and the radiation-chemical yields G are $V = GP$ and $V_1 = \varepsilon_1 G(^{\bullet}CH_2OH)P$, where P is the ionizing radiation dose rate, ε_1 is the electron fraction of methanol in the reaction system [18], and $G(^{\bullet}CH_2OH)$ is the primary yield of the hydroxymethyl chain-carrier radical – initiation yield.

IV. CONCLUSION

The mechanism and kinetics are developed for the initiated non branched-chain formation of ethanediol in methanol–formaldehyde solutions. The quasi-steady-state treatment of the reaction network suggested here yielded a rate equation describing the non monotonic (peaking) dependence of the ethanediol formation rate on the concentration of the free (unsolvated) form of dissolved formaldehyde.

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Task Allocation and Associated Protocol in E-RTA

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Abstract— *Agents in E-RTA possess the organizational knowledge that only specifies the list of agents that currently belong to its organization. For joint problem solving agents need to identify team members and do not maintain explicit models of other agents' capabilities. Task allocation protocol's aim is to formulate an automated method for agents to find a 'suitable' agent who is 'available' to perform collaborative task.*

It is necessary to ensure that the activities of agents always remain coordinated and Joint intentions guide problem-solving activity and play a key role in guaranteeing coordination among agents within an organization in complex and dynamic environments. We also assume that agents possess any time solutions to goals. This is done so that an executing goal can be terminated before its normal completion to avoid priority conflicts of requests.

This paper described the task allocation & protocols used for our proposed framework E-RTA. This complete paper described introduction in section 1, task allocation in section 2 in detail. Section 3 deals with temporal conflicts resolution method among intentions. Section 4 describes the results of our experiment and finally conclusion in section 5.

Keywords— E-RTA, Joint Problem, Task allocation protocol, problem-solving activity.

I. INTRODUCTION

In Multi-Agent-System solving a pool of requests could be in form of different formations i.e. organizations of different agents to balance load and coming rate of requests. In our proposal we aimed to reorganize those formations dynamically during new request or to maintain load.

Problem solving requests arrive at each of these organizations. A request that arrives at an organization is solved cooperatively by agents within that organization and independently of the other organizations. As the rate of arrival of problem solving requests at each of these organizations varies with time, there could be a situation where some organizations may have surplus resources, while others have insufficient resources and thereby turn down problem solving requests. In order to minimize these lost requests, the allocation of resources (agents) to organizations is changed dynamically using the microeconomic approach. This reallocation of resources changes the number of agents in the organizations and their skills, and is intended to balance the demand for resources at each organization with its supply.

But it is necessary to pose the following challenges to the MAS reorganization builder.

- Agents must be able to
  - Adapt to unpredictable changes in problem solving environment, for instance when new information becomes available, it may invalidate existing beliefs or goals and
  - Focus on higher priority tasks.
- The multi-agent system must be able to
  - Adapt to changes in load by diverting resources where they are needed most and
  - Add new agents for problem solving in an incremental manner

and thereby reorganize itself dynamically.

1.1 Previous Work

This section explores some of the existing mechanisms for implementing organizational policies. Some of the existing formalisms for implementing organizational policies in multi- agent systems are hierarchical organization, contract nets, social reasoning mechanism, and the use of economic methods.

1.2 Hierarchical Organization

In a hierarchical organization, decision-making and control is concentrated in a single problem solver at each level in the hierarchy. Interaction is through vertical communication from superior to subordinate agent. The subordinate agents have no autonomy. It is the superior agents that exercise control over resources and decision- making [30, 29, and 7]. Hierarchical organizations are therefore not suited for autonomous agent interactions.

Kumar et al. in [36] proposed the agent based layered framework for resource allocation. The framework mainly depends on one of the information retrieval technique name called vector space model. The implementation shows by using vector space model implementation as agent using JADE. The two vectors (Query and Total Availability of resources) are given as input and the framework provides the similarity coefficient for the data centers related to specific query.

1.3 Contract Net Protocol

Contract net protocol [8,31,9] achieves opportunistic and adaptive task allocation among a collection of problem solvers using a framework called negotiation based on task announcement, bids, and awarded contracts.

Cheng and Ishida [8] investigated the various effects of mutual selection mechanisms on manager and contractor utilities, their analysis (based on queuing theory) produced the following conclusions.

Sandholm [10] describes a variant of the contract net protocol for e-commerce in which tasks can be clustered to allow individual agents to bid for complementary tasks as bundle further extensions were made by Sandholm and Lesser [11,12] where decornmitments and decommitment penalties were introduced.

Other applications of contract net protocol includes Enterprise [13], the transportation control system TRACONET [10] and factory floor operations [14].

1.4 Social Reasoning Mechanism (SRM)

This model is based on social power theory [15, 16]. In the SRM model [17,18, 19,20,21,22] dynamic coalitions are formed on the basis of motivation in the form of social dependence relations. In SRM, agents maintain models of acquaintances in a data structure called external description (ED). An ED contains the agent's goals, plans, actions, and resources.

The Mobile Agent is also an option to enhanced adaptability. The paradigm of mobile has two general goals: reduction of network traffic and load balancing. It is majorly being used in enhancement of telecommunication services [32, 33].

Agent cloning [25, 26] is also proposed as a more general approach to agent mobility. In order to obtain a truly adaptive organizational policy we require a complete and comprehensive framework that does the following

- Considers criticality of tasks,
- Allows individual agents to be adaptive, and also
- Allows the multi-agent system to dynamically reorganize itself.

As agents operate in environments where they neither have complete nor correct beliefs about the environment / other agents, it is indeed essential for every agent to have the capability to engage in collaborative problem solving. However, as we are interested in situations with varying problem solving load, it is not enough if individual agents possess team rationality. There should also be a means of having the entire multi - agent system alter its organization in accordance with these variations and continue to provide services as per requirements, always giving preference to higher priority tasks in case of temporal conflicts. A comprehensive framework that satisfies all the above requirements is not available.

II. TASK ALLOCATION

2.1 An overview

At each organization accepts the problem solving requests with priorities and deadlines. The requests arriving at an organization are processed cooperatively by the agents of that organization and independently.

For a joint activity establishment, an agent must firstly recognize the need. The agent who does this, is deemed the manager or organizer. Each social action has one organizer and at least one team member called the contractor- an acquaintance who has agreed to participate. The manager's role involves obtaining a recipe, from the planner, contacting all the other agents of its organization to identify team members, determining when the actions will be performed and matching the team members with the actions to be performed.

It is a case of individual problem solving, if a goal can be achieved solely by the agent that receives it from the environment. Recognizing that a goal cannot be achieved all by itself puts the agent in an organizer's or manager's role it then has to seek team members or contractors.

Once the need for joint action has been ascertained, the responsibility model requires the following conditions to be fulfilled before it can commence, other agents who are willing to participate and are able to contribute something must be identified, the fact that a common solution is required needs to be acknowledged, participants must agree to obey the responsibility code of conduct. Finally the common solution by which the social goal will be attained must be developed.

The task allocation protocol does the following tasks

- Identification of team members in order to achieve a social goal, and
- Development of a common solution that is mutually acceptable to the organizer and the team members

As the organizer has a recipe, which specifies the sub-tasks and their temporal orderings, development of a common solution involves finding the actual time at which the sub-tasks can be executed. The fact that agents in a team will obey the responsibility code of conduct is implicit.

Our main target here is to develop a task allocation protocol for OMAS (open multi agent systems), where agents dynamically enter and leave the system. It is therefore difficult for agents to always maintain a correct model of others' capabilities. For such conditions, ensuring that each listed conditions is satisfied separately before the commencement of collaborative problem solving, involves a high degree of agent interaction and slow down the speed of operation. To attain this difficulty, the protocol that we propose settles more than one condition in a single message interchange.

Finding a team member and making them agree upon a suitable time is done for every unit-task of the recipe in the temporal order specified by the planner. Priorities are used to resolve any temporal conflicts that arise with already existing commitments, during this process. The lower priority task is either rescheduled to accommodate a more critical task. Deadlines therefore ensure termination of the specified method or the protocol.

Ensuring coordination among team agents, all social activity is represented as a joint intention, which includes the list of team, their roles and the common solution. If an agent decommits a sub-task, it notifies all associated team members. This keeps the entire team aware of the current state of problem solving activity and results in all team members either together progressing on the solution, or jointly dropping a goal if it is not suitable.

The protocol proposed here is time bonded, the planner determines if an anytime solution is available for the sub-t If tasks, it associates a minimum amount of time that needs to be spent for obtaining a meaningful solution. On time elapses, execution of the unit task can be terminated to accommodate more critical requests, else continued to completion.

2.2 The protocol

Following assumptions, one, it is assumed that the communication is foolproof and that the message delay time is known to all agents. Two, in order to carry out task allocation activity, agents share a global clock reference. Next, agents are able to accurately predict the time taken in terms of the global clock, to execute each domain level task. This facilitates the task allocation process and enables agents to make and admiration commitments in a convenient manner.

The following notation is used in the discussion that follows

a_i i^{th} action

A_i i^{th} agent

G_i i^{th} goal

T_i the time at which action i is executed

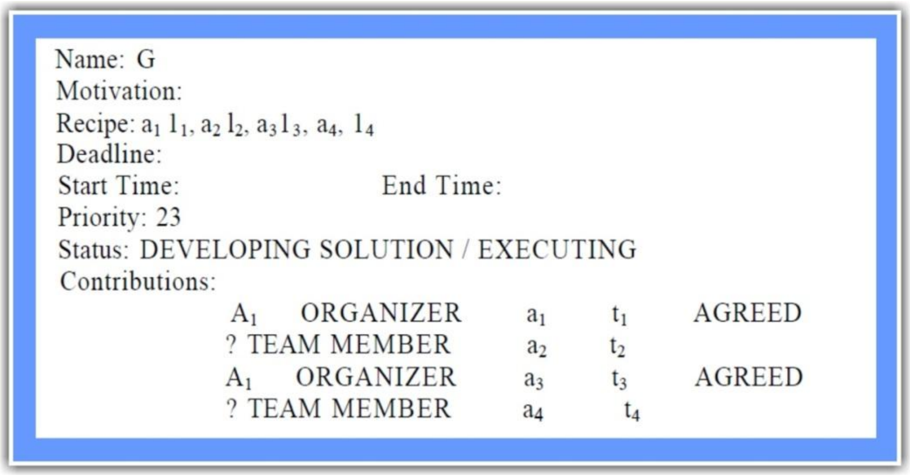
The organizer instantiates a representation of the social goal as a joint intention, in its self-model, as in Figure 1. The motivation slot indicates the reason for carrying out the joint intention.

The recipe is a series of actions, which need to be performed together with some temporal ordering constraints, which will produce the desired outcome. Figure 1 showing actions, a1, a2, a3, a4, are temporally ordered. The values l1, l2, l3 and l4 indicate the lower bounds on execution time for each of the actions, since actions are assumed to have an anytime solution. This method is however not limited to actions having anytime solutions. If an anytime solution is not available, then li is the fixed period of time that needs to be spent for obtaining the solution. The formulated plan indicates what is to be done and in what order, not who is to do it nor the exact time at which it should be done.

Problem solving requests are assumed to arrive with an associated deadline If an incoming request does not have an associated deadline, E-RTA associates a default deadline with it. This is done to ensure termination of the task allocation process.

For starting and ending the joint activity, the start time and end time indicate the commonly agreed time. The priority slot indicates the local agent's assessment of the importance of the intention and is used as the basis for computing its disability.

The status slot of joint action description refers to the current activity of the task allocation protocol and has the value establishing group & developing solution' or 'executing joint goal'. Contribution slot records those agents that are capable of contributing and have agreed to the joint action. Initially the organizer, agent A1, has agreed to contribute by performing the actions a1 and a3. No other agent has yet agreed or even been asked to contribute anything. Contractors now need to be found for performing a2 and a4.

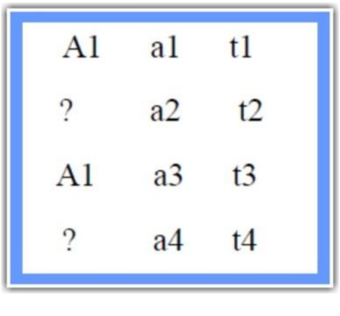


Name: G
Motivation:
Recipe: $a_1\ l_1,\ a_2\ l_2,\ a_3\ l_3,\ a_4,\ l_4$
Deadline:
Start Time: End Time:
Priority: 23
Status: DEVELOPING SOLUTION / EXECUTING
Contributions:

A_1	ORGANIZER	a_1	t_1	AGREED
?	TEAM MEMBER	a_2	t_2	
A_1	ORGANIZER	a_3	t_3	AGREED
?	TEAM MEMBER	a_4	t_4	

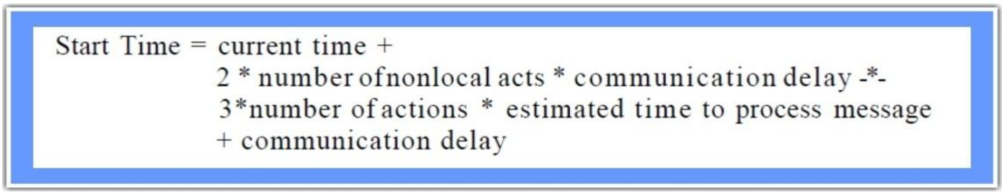
FIGURE 1: View of joint intention

After identifying the need for joint goal, the process of establishing it and arming at a common solution can commence. This requires finalizing the detailed timings and duration of the actions. The team leader prepares an initial proposal for the individual action timings and fills in the joint goals duration and its start and end times in the joint intention



A1	a1	t1
?	a2	t2
A1	a3	t3
?	a4	t4

The fact that some time is required to agree to the solution, work cannot commence immediately and formula for time lag is given below. It takes the following factors into consideration, for each action which needs to be performed by an acquaintance at least two messages must be transferred i.e. announcement to all agents of the organization and bid to the organizer, to establish its start time. An agent takes time to process a message and then an award message must be sent to all team members when the solution is agreed upon.

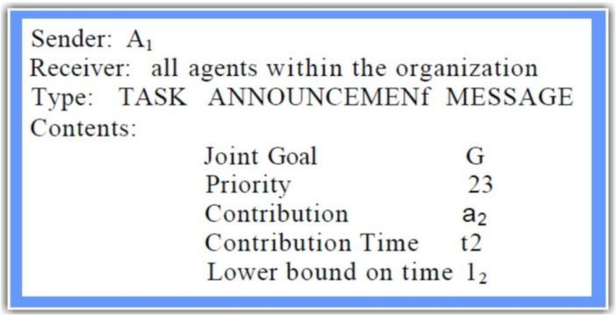


Start Time = current time +
2 * number ofnonlocal acts * communication delay -*-
3*number of actions * estimated time to process message
+ communication delay

There is no complete picture, of the capabilities of other agents within the organization, for the team organizer. Hence, the organizer does not know the existing commitments and desires of all its potential team members, so neither actions nor their exact timings can be dictated, they have to be negotiated, and to avoid disordered behavior and many iterations, the organizer takes each action in the recipe in a temporally sequential order. It is to be considering that only the task allocation is done sequentially - the tasks can be executed in parallel or overlapped if the plan has been so defined.

Consider a case where t1=12, t2=16, t3-21, t4=25, for each action the organizer negotiates with the prospective team members, other agents of the organization, the appropriate time at which it should be performed. Thus action a2 is negotiated first, and a time is agreed which fits in with the existing obligations of the prospective team member and the organizer's rating of the action's desirability. Then A1 finds a suitable time for a3 and so on for each of the actions.

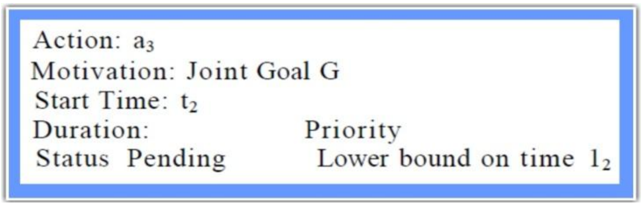
As agents do not maintain models of other agents that represent their capabilities, the organizer describes the task to the entire, by broadcasting a task announcement message This message, as in figure 2, indicates that the sender wishes to establish a joint goal and arrive at a common solution involving the recipient, states the team organizer's priority for the task, the action for which a contribution is required the time at which the action needs to be started, and a lower bound on execution time, that the prospective team member is expected to spend for that action.



Sender: A_1
Receiver: all agents within the organization
Type: TASK ANNOUNCEMENf MESSAGE
Contents:
Joint Goal G
Priority 23
Contribution a_2
Contribution Time t2
Lower bound on time l_2

FIGURE 2: Task allocation message format

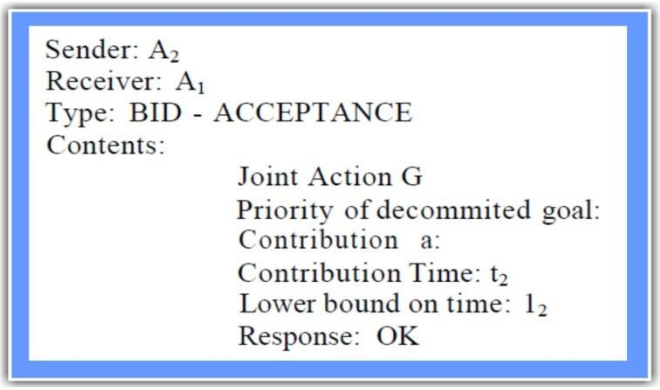
Upon receipt of proposal the team members evaluate it to see whether it is acceptable; refer to Section 3 for further details of this process If there is no conflict, the agent sets up a joint intention similar to that of Figure 1, and an individual intention as shown in Figure 3 The motivation slot indicates the goal for which contribution is required The status slot is 'pending'.



Action: a_3
Motivation: Joint Goal G
Start Time: t_2
Duration: Priority
Status Pending Lower bound on time l_2

FIGURE 3: Individual Intentions for Agent A2

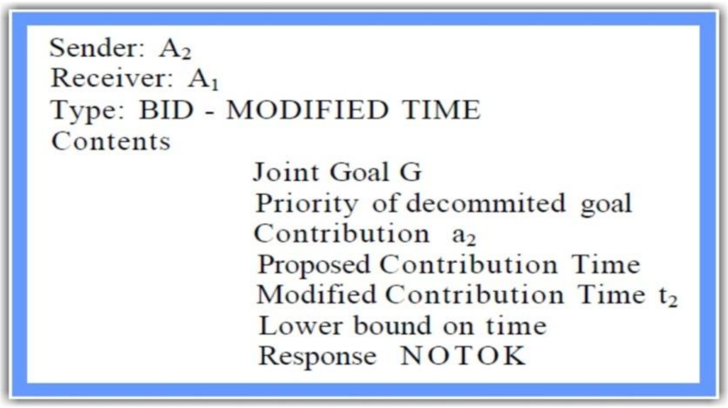
Agents then return a message indicating their acceptance to the team organizer, figure 4. The 'priority of decommited goal' slot indicates whether the prospective team member is able to accommodate the request BV decommiting a pre-existing lower priority goal, and if so, the priority of that goal. The organizer can use this information as the basis for selecting a team member during the bid evaluation process.



Sender: A_2
Receiver: A_1
Type: BID - ACCEPTANCE
Contents:
Joint Action G
Priority of decommited goal:
Contribution a:
Contribution Time: t_2
Lower bound on time: l_2
Response: OK

FIGURE 4: Acceptance bid message

If time is unacceptable, the prospective team member proposes a time at which the action can be fitted in with its existing commitments, makes a tentative commitment for this time and returns the suggestion to the organizer, figure 5. If the modified time is acceptable to the organizer, it will make appropriate adjustments to the subsequent solution timings and proceed with the next action. If the modified time proposal is unacceptable, the organizer will look for a new agent to perform the action from its list of proposed contributors.



Sender: A_2
Receiver: A_1
Type: BID - MODIFIED TIME
Contents
Joint Goal G
Priority of decommited goal
Contribution a_2
Proposed Contribution Time
Modified Contribution Time t_2
Lower bound on time
Response NOTOK

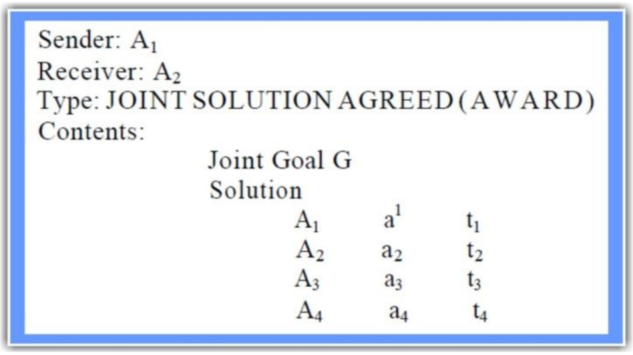
FIGURE 5: Modified time bid message

Among the agents willing to participate, the organizer selects as team member the agent that can perform the task earliest. If there is more than one agent that can perform the task, the organizer selects the one which can perform it by decommiting the lowest priority task.

The process of agreeing at a time for each action continues until all actions have been successfully dealt with. At this point the common solution is agreed upon and the organizer informs all the team members of the final solution by means of an award message as figure 6.

The joint intention status slot is changed to 'executing-joint-action' and the contribution slot is updated to indicate that all team members have agreed to the goal, and a common solution and implicitly to the responsibility code of conduct, and are now in the process of executing the joint action. The status slot in the individual intention is also changed to 'executing'. On receiving the award message, the team members also make similar changes to their joint and individual intentions and become contractors for that goal. All the preliminaries for joint action have been satisfied and group action can begin.

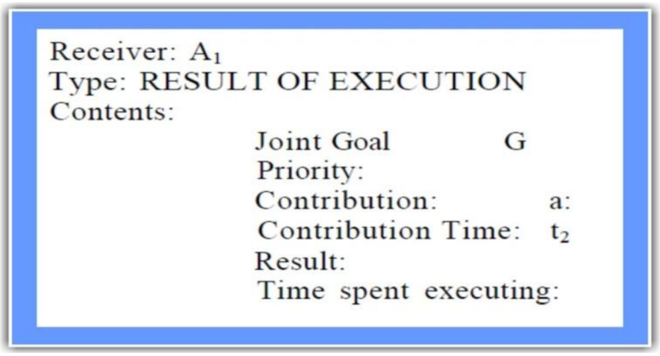
After completing an allocated task, the team members report the results of execution to the organizer, as Figure 7.



Sender: A_1
Receiver: A_2
Type: JOINT SOLUTION AGREED (AWARD)
Contents:
Joint Goal G
Solution

A_1	a^1	t_1
A_2	a_2	t_2
A_3	a_3	t_3
A_4	a_4	t_4

FIGURE 6: Start of Joint Action (Award Message) notification



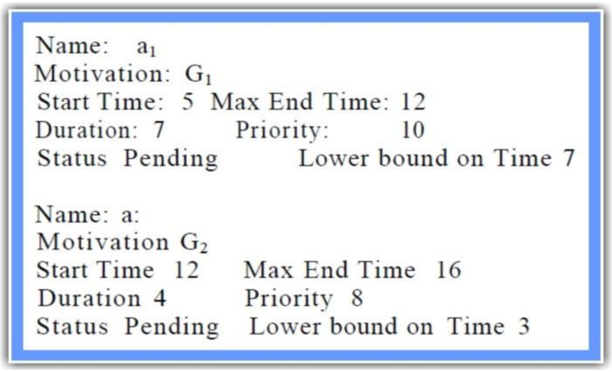
Receiver: A_1
Type: RESULT OF EXECUTION
Contents:
Joint Goal G
Priority:
Contribution: a:
Contribution Time: t_2
Result:
Time spent executing:

FIGURE 7: Execution result

2.3 Temporal incompatibilities resolution

In order to exhibit correct behavior, agents need to ensure that their intentions always remain compatible. Two intentions are said to be incompatible if the times for which they are scheduled overlap, they are compatible if they are distinct. Consider an agent having two intentions for tasks a1 and a: represented in its self-model (Figure 8). These two intentions are compatible because the times at which they are carried out, 5 to 12 and 12 to 16 do not overlap.

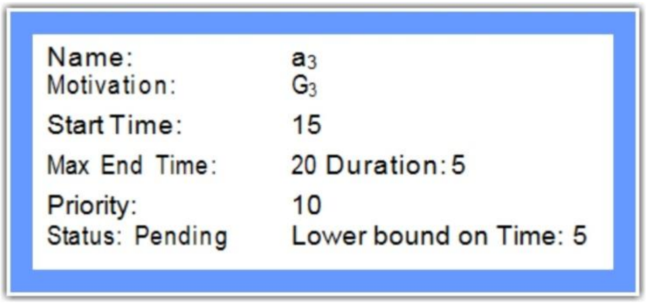
Before the commencement of their execution a new request arrives that corresponds to the intention as Figure 9.



Name: a_1
Motivation: G_1
Start Time: 5 Max End Time: 12
Duration: 7 Priority: 10
Status Pending Lower bound on Time 7

Name: a:
Motivation G_2
Start Time 12 Max End Time 16
Duration 4 Priority 8
Status Pending Lower bound on Time 3

FIGURE 8: Consistencies of Intentions



Name: a_3
Motivation: G_3
Start Time: 15
Max End Time: 20 Duration: 5
Priority: 10
Status: Pending Lower bound on Time: 5

FIGURE 9: New Intentions

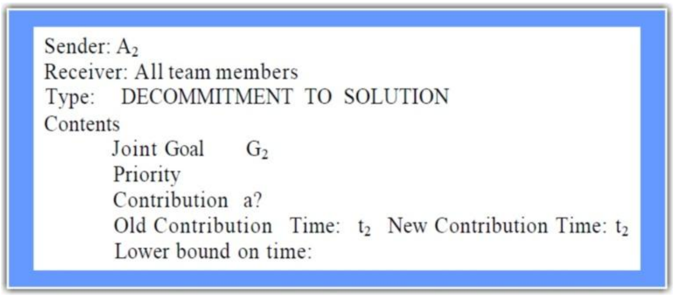
The inconsistency resolver now has to determine whether the new proposal is compatible with the agents existing intentions. As a result of this analysis the inconsistency resolver will indicate that the new intention is compatible because even though the times overlap, a2 requires an anytime solution, lower bound < duration, and can therefore be accommodated with the new intention. This requires termination of a2 at time 15 in order to start a3.

In case an anytime solution is not available for a2, then it becomes incompatible with a3. The inconsistency resolver resolves this by making use of the priority values for each of the intentions. If the new request is less desirable than the existing commitments, then the agent proposes a modified time that can be fitted in with the existing commitments. In the above example however, a3 is more desirable Therefore the agent forms the intention to achieve a3 from time 15 to 20 and reschedules a2 after a3. The new intention for a2 now becomes.

Name: a2
Motivation: G2
Start Time: 20
Max End Time: 24
Duration: 4
Priority: 8
Status: Pending
Lower bound on Time 4

The other actions of G2 that get affected due to this change also need to be rescheduled. If the new schedule for G2 does not conform to its deadline, then the agent decommits G2 and updates the number of recommitments. This is all that needs to be done if G2 is a primitive goal However if a2 corresponds to a joint goal just rescheduling a2 is not enough. The agent must inform all team members about its decommitment to the originally agreed solution as dictated in figure 10.

Upon receipt of this message, the other team members also drop commitment to the common solution. When the team organizer receives this message it reschedules G2 if possible, otherwise decommits the goal G2, informs all team members about the decommitment to the joint goal (see Figure 11), and updates the number of decommitments. In this way all organizers record information about their decommited goals and convey this information to the resource manager, which utilizes it for performing resource allocation (we will describe resource allocation protocol in our next paper as these papers are taken from our P.hd. thesis work).



Sender: A_2
Receiver: All team members
Type: DECOMMITMENT TO SOLUTION
Contents
Joint Goal G_2
Priority
Contribution a?
Old Contribution Time: t_2 New Contribution Time: t_2
Lower bound on time:

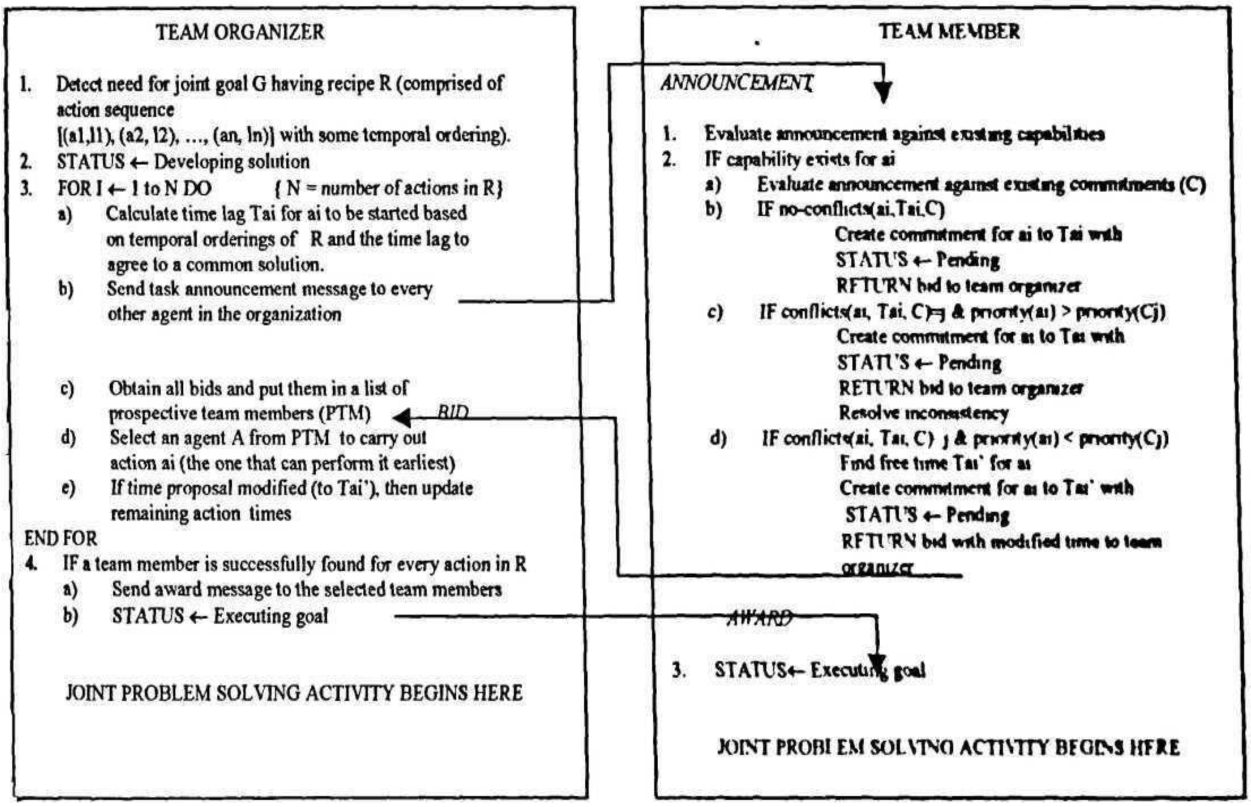
FIGURE 10: Decommitment to solution Message

Sender: A_1
Receiver: All team members
Type DECOMMITMENT TO JOINT GOAL
Contents
Joint Goal G_2
Priority
Contribution a_2
Contribution Time
Lower bound on time

FIGURE 11: Decommitment to joint goal message

III. EXPERIMENT

The inclusion of anytime solutions results in a considerable improvement in the performance of agents. This can be demonstrated by an experiment as Figure 13. The protocol was implemented in Java and run for two organizations of five agents each. Agents in one organization used anytime algorithms and agents in the other used standard algorithms. Several problem-solving requests were made randomly to each of these organizations, half of which were assumed to have anytime solution. The organizations can handle requests (without decommitments), if they arrive at intervals of 16 or more If the frequency of requests increases, the number of decommitments also increases correspondingly. The performance was measured in terms of the goals that were decommited. Since "anytime" algorithms can provide 'some' solutions even in lesser time, the agent can take up other goals if required. As a result, the number of decommitments is far less compared to the organization with standard solutions.



```
TEAM ORGANIZER

1.  Detect need for joint goal G having recipe R (comprised of
    action sequence
    [(a1,l1), (a2, l2), ..., (an, ln)] with some temporal ordering).
2.  STATUS ← Developing solution
3.  FOR I ← 1 to N DO          { N = number of actions in R}
    a)  Calculate time lag Tai for ai to be started based
        on temporal orderings of  R and the time lag to
        agree to a common solution.
    b)  Send task announcement message to every
        other agent in the organization

    c)  Obtain all bids and put them in a list of
        prospective team members (PTM)
    d)  Select an agent A from PTM  to carry out
        action ai (the one that can perform it earliest)
    e)  If time proposal modified (to Tai'), then update
        remaining action  times
END FOR
4.  IF a team member is successfully found for every action in R
    a)  Send award message to the selected team members
    b)  STATUS ← Executing goal

    JOINT PROBLEM SOLVING ACTIVITY BEGINS HERE
```

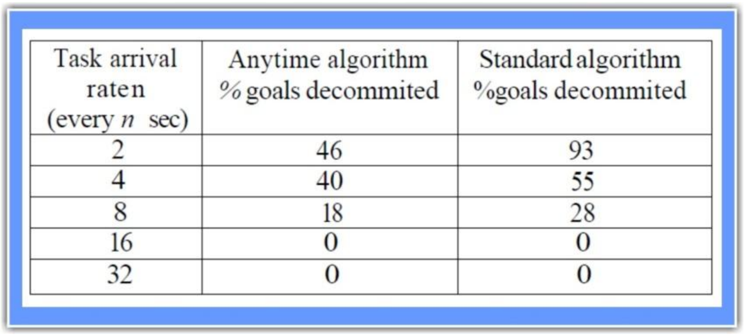
```
TEAM MEMBER

1.  Evaluate announcement against existing capabilities
2.  IF capability exists for ai
    a)  Evaluate announcement against existing commitments (C)
    b)  IF no-conflicts(ai,Tai,C)
            Create commitment for ai to Tai with
            STATUS ← Pending
            RETURN bid to team organizer
    c)  IF conflicts(ai, Tai, C)=j & priority(ai) > priority(Cj)
            Create commitment for ai to Tai with
            STATUS ← Pending
            RETURN bid to team organizer
            Resolve inconsistency
    d)  IF conflicts(ai, Tai, C) j & priority(ai) < priority(Cj)
            Find free time Tai' for ai
            Create commitment for ai to Tai' with
            STATUS ← Pending
            RETURN bid with modified time to team
            organizer

3.  STATUS← Executing goal

    JOINT PROBLEM SOLVING ACTIVITY BEGINS HERE
```

FIGURE 12: Allocation protocol



Task arrival raten (every n sec)	Anytime algorithm % goals decommited	Standard algorithm %goals decommited
2	46	93
4	40	55
8	18	28
16	0	0
32	0	0

FIGURE 13: Performance of agents using anytime and standard solutions

IV. CONCLUSION

This paper describes the main protocol for task allocation used in our proposed framework E-RTA. All allocation requested tasks have an associated time binding and priority so that higher priority tasks are executed in time by the assigned agents. Even, a situation could arise where an organization is overloaded as the computational load on any organization of the MAS is unpredictable; but the MAS as a whole has the required resources to take on that load.

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