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VIEWS

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Agricultural Education: Intellectuals and Strategies for Ensuring Peace, National Unity and Sustainable Development in the 21St Century

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ABSTRACT

The paper examined the transformation of agricultural education and the implications for food security in Nigeria. The paper argued that the level of hunger in Nigeria was minimal at independence because majority of the people engaged in agriculture. The discovery of crude oil in the 1970s and subsequently exportation contributed over 90% to government revenue. This enabled government to embark on massive projects which injected much money into the economy. This led to abandonment of agriculture to the rural poor who continue to use crude implements. The result is food insecurity and hunger resulting in mal-nutrition and disease in many homes. The paper further argued that one sure way to transform the agricultural sector and ensure food security is adequate education of the populace on the use and application of agricultural tools and implements. Consequently, the way forward for agricultural transformation in Nigeria is suggested.

Keywords: Sustainability, enduring peace, nation, unity, century.

Introduction

Nigeria has a highly diversified agro-ecological condition, which makes possible the production of a wide range of agricultural products such as cocoa, ground nut, palm produce etc (Modebelu and Nwakpadolu, 2013). The citizens could complain of poverty but not extreme hunger. This could be probably because virtually everybody was in one way or the other involved in agricultural activities. Although, the practice appeared crude and unnecessary energy sapping due to crude implements in use and inadequate application of modern agricultural practices, but it indeed, ensured availability of food. Agriculture then seemed sustaining because everybody was involved, everybody had interest and it appeared to be everybody's major source of family sustenance. Consequently, there were less cases of unemployment due to less interest or crazy for white collar jobs. Thus, the sector is particularly important in terms of its employment generation and its contribution to Gross Domestic Product (GDP) and export revenue earnings.

However, despite Nigeria's rich agricultural resource endowment, the agricultural sector has been growing at a very slow pace. For instance, less than 50% of the country's cultivable agricultural land is under cultivation (Manyong, Ikpi, Olayemi, Yusuf, Omonona, Okoruwa and Idachaba, 2005). This is even as smallholder and traditional farmers, who use rudimentary production techniques with resultant low yields, cultivate most of this land. The smallholder farmers are constrained by many problems including those of poor access to modern inputs and credit, poor infrastructure, inadequate access to markets, land and environmental degradation, and inadequate research and extension services (Manyong et al., 2005). Also, the advert of the oil boom led to complete diversion of the citizens and national interests from agriculture as source of income. The citizens now loss interest in agricultural practices because it is treated as business for the less privileged and peasants in the rural areas etc. The repercussions are that agricultural practices has been deserted, hunger and poverty have taken over.

Consequently, food security is now the order of the day, especially at this era of incessant occurrence of various forms of natural disasters such as flood, erosion, desertification etc. The only way forward is re-embracing agriculture as a veritable source of income, food, employment, hobby, tourism etc. This is while majority of third world nations are leaving no stone unturned in repositioning their agricultural sector. They see it as one sure way of eradicating extreme poverty and hunger as recommended in millennium development goals (MDGs). Food security is one sure way to meet up with this number one goal of MDGs.

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Ostensibly, increase in the incidence and severity of poverty in Nigeria is predicated on the dwindling performance of the agricultural sector where majority of the poor are employed. Furthermore, poverty in Nigeria has been assuming wider dimensions including household income poverty, food poverty/insecurity, poor access to public services and infrastructure, unsanitary environment, illiteracy and ignorance, insecurity of life and property and poor governance. In response to the dwindling performance of agriculture in the country, governments have, over the decades, initiated numerous policies and programs aimed at restoring the agricultural sector to its pride of place in the economy. However, no significant success has been achieved due to the several persistent constraints inhibiting the performance of the sector (Manyong et al., 2005). From the perspective of sustainable agricultural growth and development in Nigeria, the most fundamental constraint is the peasant nature of the production system with its low productivity, poor response to technology adoption strategies, poor returns on investment and poor or inadequate education programme on agriculture.

To ensure transformation of agriculture activities in Nigeria, it is imperative that those constraints inhibiting the performance of the sector are first identified with a view to unlocking them and creating a conducive investment climate in the sector through enlightened education programmes, such that, agriculture will become one of the most important growth points in the economy. It is against this backdrop that the study is undertaken. The rest of the paper is structured as follows. Section two undertakes brief conceptual literature as well as overview of agricultural transformation in Nigeria. In section three, some factors inhibiting agricultural sector growth were identified. Section four contains ways forward for food security in Nigeria while section five concludes the paper.

Conceptual Literature

Agriculture can be defined as the practice of cultivating the soil and raising livestock to produce plant and animals useful to humans and in some instances animals (Asoegwu and Asoegwu, 2007). According to Udoh (2000), agriculture is the economic mainstay of the majority of households in Nigeria and is a vital sector for the economy. The important benefits of the agricultural sector to Nigeria's economy include: the provision of food, contribution to the gross domestic product, provision of employment, provision of raw materials for agro-allied industries and foreign exchange earnings (Oni, Nkonya, Pender, Philips and Kato, 2009).

On the other hand, food security refers to a situation where a nation has ready food to consume in their reserves. This is while Abbey (2011), argues that food security is a situation where all the individual, household, national, regional and global levels at all times have physical and economic access to sufficient safe and nutritious food to meet their dietary needs and food preference for active and healthy life. Sort (2001) describes food security as a world where person has access to sufficient food to sustain a healthy and productive life, where malnutrition is absent and where food originates from efficient, effective and low-cost food systems that are compatible with sustainable use of natural resources. Achor (2003) observes that food security is one of the major challenges facing the third world nations. He discovers that government inability to provide sufficient food for its ever increasing population has been the root cause of extreme poverty and hunger among the citizens.

Anyanwu and Anyanwu (2008) report that cases of food insecurity ensued due to sudden population increase which meant that the quantity of food and fruit gathered during hunting and local farming are now insufficient. They argue that it is easy to make more food available to the ever increasing populace and conclude that food security issue is not peculiar to Nigeria alone as many other developing nations are also facing acute food shortage due to population explosion, poor management of resources, inability to adapt to new technology and utilizing education to explore new challenges.

Overview of Nigeria Agricultural Policies

A number of agricultural policies have been formulated in Nigeria before and after independence. In the Colonial Ten Year Development Plan (1946–1956), the commodity crop production emphasized was mainly oil palm, cocoa, rubber, cotton and groundnuts. The document contained very little or no proposal for increased food production. After independence, the first National Development Plan was 1962-1968. The policy sought for increase in the production of export crops through better seed distribution and more modern methods of cultivation as well as through the increase in area under cultivation. Consequently, farm settlements and cooperative plantations as well as Tractor Hiring Units were established and agricultural extension services were greatly expanded (Asoegwu and Asoegwu, 2007). This Plan Period was a success as cash crops accounted for about 80% of total export and 45% of the gross domestic product (GDP). However, no mention was made of the food sector in this plan that had 11.6% capital allocation by both Federal and State Governments to Agriculture (Osakwe and Ojo, 1986).

In the period1970-74, the government launched The Second National Development Plan during which the National Agricultural and Cooperative Bank (NACB) was established in 1973 to facilitate agricultural financing to farmers. Also, the National Accelerated Food Production Programme (NAFPP) was initiated which laid emphasis on agricultural research and extension support to farmers. However, with massive exploration of crude oil which contributed over 98% to total export and 73% of GDP, the agricultural policies and programmes were clumsily executed and virtually abandoned by succeeding military regimes (Opara, 2006). Consequently, capital allocated to agriculture for crop production, irrigation, research, credit (loans or subsidy), mechanization, man-power and agricultural extension services, declined (Osakwe and Ojo, 1986). For instance, the cocoa plantations suffered serious setback, the cotton and groundnut pyramids disappeared, hides and skin became food for the embattled Nigerian populace, and the oil palm plantations which were battle fields during the Biafra/ Nigeria Civil War died natural death due to neglect. The disaster on agriculture and food production was enormous and the effect on Nigerians has not been ameliorated till date (Asoegwu and Asoegwu, 2007).

The Third National development Plan (1975-80) was the first to spell out provisions for food security because of serious deficit in food production. In 1976, the Operation Feed the Nation (OFN) programme was inaugurated to create awareness among Nigerians about the consequences of an empty national food basket. Also, a number of Marketing Boards were abolished and Production and Marketing Companies were established. There was also the establishment of River Basin Development Authorities (RBDAs), Agricultural Development Projects (ADPs) and many research and tertiary institutions among others were established with the aim of improving agricultural food production (Asoegwu and Asoegwu, 2007). However, there was no commensurate capital allocation to Agriculture and this led to decline in food production (Osakwe and Ojo, 1986).

The Fourth National Development Plan (1981-85) saw the emergence of the Green Revolution which tried to give more powers and impetus to the River Basin Development Authorities and the ADPs to produce more food for the nation with more capital allocated to the agricultural sector (Osakwe and Ojo, 1986). Even though these efforts seemed to have been guided by genuine concerns, they failed to make the necessary impacts in the agricultural sector because of fundamental structural problems in the economy. According to Asoegwu and Asoegwu (2007), agricultural sector contribution to GDP declined by about 20% during the period. This resulted in increased shortage of food as evidenced by increased food imports and increased high prices (Asoegwu and Asoegwu, 2007).

Experience from the three National Plan Periods convinced Government that there can be no alternative to well-designed and articulated agricultural policies as instruments for promoting agricultural growth and development in Nigeria (Igbeka, 2003). In 1988, the Federal Government published the first ever agricultural policy document for Nigeria aimed at redressing the underdevelopment of agriculture, streamlining policies in all tiers of government and ensuring policy stability (Opara, 2006). However, many factors worked against the implementation of this policy. They include poor funding and poor state of infrastructure, poor administration of government support to agriculture and abandonment of projects midstream due to political reasons; lack of appropriate technology to reduce drudgery in agricultural production and processing and inadequate availability of inputs such as improved seeds and breeding stock among others (Asoegwu and Asoegwu, 2007).

In the periods between 1992-1998, succeeding governments saw that women involvement in agriculture was high and as such government policies were centered on women. Thus, programmes such as Better Life for Rural Women; Family Support Program (FSP); Family Economic Advancement Programme (FEAP) were initiated. These were meant to empower the women for more and better involvement in agriculture and other rural activities in order to enhance the production of food and agricultural raw materials.

The current democratic dispensation began 1999 and the various governments till date have implemented different reform programmes ranging from privatization, commercialization, deregulation to corruption and financial crimes. These are meant to stabilize the economy and make it more productive; ensuring that the era of subsidies and over-protection of key sectors of the economy including agriculture is over (Van Otterdijk, 2005). In 2001 - 2010, New Agricultural Policy was introduced and in order to fast track the gains of the policy, government set up Presidential Initiatives in Agriculture (PIA) in 2004 and the National Special Food Security Program (NSFSP) and FADAMA II in 2005. At the moment, there are NSFSP and FADAMA I, II and III, all targeted at raising agricultural productivity and production as well as food security and eliminate poverty among resource poor rural farmers.

Starting in 2010 – 2011, the Government of Nigeria, after years of benign neglect, began to reform the agriculture sector. To refocus the sector, the Government implemented a new strategy (the Agricultural Transformation Agenda, ATA) built on the principle that agriculture is a business and therefore policy should be about supporting it. The main priority of the policy was to “restart the clock” and reintroduce the Nigerian economy to sustainable agriculture centered on business-like attitude driven by the private sector. That strategy was in place from 2011 – 2015. The ATA was a good platform to re-engage key stakeholders in Nigerian agriculture to shift focus towards how a self-sustaining agribusiness focused economy could be built. The ATA focused on how to make Nigeria’s agriculture more productive, efficient and effective. It set a target of creating 3.5 million jobs by 2015; generating foreign exchange, and reducing spending on food imports. Among its key achievements was a restructuring of the federal fertilizer procurement system. On balance, the ATA was an important first step towards rediscovering agriculture. As a result, many companies, individuals and donors are now keen to invest in Nigerian agriculture once again. Agriculture is viewed as a business that can provide a reasonable basis for further wealth and job growth in Nigeria. With that in mind, the policy and strategic focus is now on how to build on the initial progress made, and transition of Nigeria to a new plane in terms of agribusiness performance. That will be the focus of the proposed new policy regime. That new policy's primary focus will be on closing the demand – supply gaps between crop and livestock production. Gap closing will also include tackling related input, financing, storage, transport and market access issues present in key value chains.

According to Audu(2016), building on the successes and lessons from the ATA, the vision of the Buhari Administration for agriculture is to work with key stakeholders to build an agribusiness economy capable of delivering sustained prosperity by meeting domestic food security goals, generating exports, and supporting sustainable income and job growth. In this regard, a number of specific objectives for the period 2016 – 2020 emerge.

Therefore, in 2016 to 2020, Nigeria's policy now needs to be readjusted to solve the agricultural challenges. The go forward, federal priorities (in partnership with State Governments) will be the following four: food security; import substitution; job creation; and economic diversification. The new policy regime, tagged the **AgriculturePromotionPolicy(APP)** is founded on the following guiding principles, a number of which are carryovers from the ATA reflecting the strong desire for policy stability. New elements added reflect the lessons from the ATA, as well as priorities emerging from the aspirations of the Buhari Administration. (Audu, 2016).

Trends in Agricultural Education and Training

In Africa in general and Nigeria in particular, food security is still a critical issue and therefore food production will continue to be a major focus of agricultural education and training institutions for some time to come. African agriculture has gone through considerable changes over the years and a number of these changes are unfolding. Some of the emerging trends and developments affecting agriculture and agricultural education in Africa include but not limited to the following:

Shift in Focus from Agriculture to Rural Development: One of the challenges to post-primary agricultural education in Nigeria is how to meet the challenge of providing education and training for rural development rather than for agriculture alone. It is clear that the older curricula which concentrated on agriculturalproduction only are no longer able to produce educated people who can deal with the wider problems of rural development. To address this problem therefore, post-primary agricultural education and training needs to be applied on practical base rather than purely theoretical. Learning needs to emphasize inductive reasoning skills so that students can interpret problems and devise solutions to them.

Rapid Population Growth Rates and Urbanization: Excessive population growth and its problematic distribution in a number of countries pose one of the greatest challenges for successful tackling of food and agricultural problems in sub-Saharan Africa (SSA). One fact that is not always recognized is that, the rapid rate of urbanization in SSA, is bound to make urban food insecurity and poverty a major problem. The rates of urban population growth in SSA in general and Nigeria in particular are among the highest in the world. It is generally agreed that rural-urban migration is the single most important cause of the explosion in the growth of the continent's urban population. As the overall population of African countries has increased at an accelerated pace, agricultural productivity has declined as the absence of appropriate technologies force farmers to start cultivating marginal lands. The results have been rapid degradation of the environment and increasing levels of food insecurity and poverty. Because of the well known urban bias in national policies, the provision of physical, social and economic services in many rural areas is often either non-existent or extremely appalling. On the other hand, the provision of these services in the urban centers, although inadequate, appears in the eyes of the rural population, to be much better. As a result, the pull of the cities becomes irresistible for many rural people, particularly the youths. Post-primary agricultural education and training institutions need to incorporate population education concepts and principles into their curricula (Vandenbosch, 2006).

Environmental Degradation and Unsustainable Water Use: Environmental constraints are already posing serious limitations to food security in several African countries particularly in areas where population densities are increasing rapidly. Today, virtually no inhabited area of Africa is unaffected by environmental degradation of one sort or another. The problem is being compounded by reduced levels and erratic patterns of rainfall and accelerated by destructive cultural practices leading to severe soil problems and loss of valuable agricultural land. Rangelands are being destroyed as a result of overgrazing and wasteful and inpropermanagement of available water resources.

Increases in Incomes and Wealth: Ironically, as the continent's resources are used to create wealth, the resulting growth in the per capita income of the poor will increase their purchasing power, upgrade the quality of their diets and create additional challenges for more food (Vandenbosch, 2006). This further aggravate the competition for land between agriculture and construction of cities, factories and roads as well as increase the demand for woodbased products, including fuel wood, lumber for construction, poles, furniture and paper. National and sub-regional markets will play more important roles due to the high population increases in cities and urban centres. This will also have implications for the continent's forests, soils, wildlife habitat and biodiversity.

PROBLEMS OF AGRICULTURAL TRANSFORMATION IN AFRICA

Soil erosion caused by water and wind is one of the main problems of agriculture in Africa. The lack of development in low-lying flood plains also hinders the development of agriculture in the continent. In addition, the dependence on imported foods has disincentive effect on investment in local farming. Specifically, some of the problems confronting agricultural productivity include:

Soil Infertility: The problems of agriculture in Africa begin with the soil. Most of the farmable land in Nigeria contains soil that is low to medium in productivity. The main problem that affects soil fertility is soil erosion. Wind erosion, in particular, is quite damaging. Overtime, strong winds expose seedlings and crop root systems by blowing away loose, fine grain soil particles. Another effect is the accumulation of soil particles in drifts, which can cover crops. Also, wind erosion changes the texture of the soil. The particles responsible for water retention and fertility, such as clay, silt and organic matter are generally lost, leaving behind a sandy soil. Wind erosion can be greatly reduced by planting trees near farming areas which will absorb most of the wind and prevent the loss of soil particles.

Poor Irrigation: The low-lying flood plains are very fertile during the rainy season, but the lack of rain during the dry season hinders agricultural development. The lack of water management systems in these areas is a concern for many agriculturalists and farmers. By adding irrigation canals and access roads to these areas, yearly production yields are expected to increase. Unfortunately, irrigation system in Nigeria is poor.

Food Processing Issues: It is estimated that about 20-40% of the yearly harvest is lost during processing. The primary cause is the lack of efficient harvesting techniques. Most farmers harvest crops by hand, instead of using machines. Also, storage methods are not generally up to standards. Most of the crops are lost to physical damage caused by insects, bacteria or fungus.

Impact of Imported Food: Africa is a net importer of food. The country does not produce enough food to meet the demand of its people. This produces a lot of problems with regard to agricultural development. Generally, there is less incentive for local farmers to grow local foods, when cheaper, more palatable foods are imported. This forces local farmers to reduce prices, which reduces the income generated by the farm. The consequence decreased farm production and food insecurity. To combat the effects of imported food on development, several initiatives are suggested, including providing farmers with micro-credit that is subsidized and increasing tariffs on imported food.

Infrastructural Inadequacies: Infrastructure here includes roads and railway system, educational and health facilities, social services such as electricity and communication system. In many parts of Africa, physical and marketing infrastructure is poorly developed, storage facilities are rudimentary and access to information and markets is highly restricted. The infrastructure constraint has persisted due to poor governance, poor political leadership, poor maintenance culture and poor funding. In terms of road facilities, the constructed roads do not often last for more than three to five years before they start to crumble due partly to poor maintenance culture. In addition, the railway system has been comatose for years thereby restricting the movement of agricultural inputs and outputs to the road transport system (Olukunle, 2013). The educational and health facilities are largely urbanbiased. Electricity supply is often epileptic and communication system is still poor. Although recent expansion of the Global System of Mobile Communication (GSM) infrastructure and Internet services has improved the communication situation somewhat, the services are urban-biased and too expensive for the average people.

Unstable Input and Output Prices: A major problem inhibiting investment in agriculture is the escalating cost of major farm inputs. Average prices of farm inputs such as hoe, matchet, sprayer, tractor and agrochemicals have been rising over the years. The rising prices of inputs are the results of instability in the factor markets arising from instability in macroeconomic policy actions leading to inflationary pressures, high interest rates and volatile exchange rate. Moreover, the rising prices of fuel have led to rising cost of transportation of farm inputs thus aggravating the rising cost of production. The situation not only made procurement difficult but again resulted in cost escalation arising from the depreciated naira exchange rate. Consequently, the rising costs of farm inputs combined with dearth of investible funds pose a serious constraint to investment in agriculture, all of which leads to food insecurity.

Challenges in Agricultural Transformation in Nigeria

According to Audu (2016), unlocking Nigeria's full agricultural potential requires that Nigeria solve the underlying challenges in its agricultural system, which includes the following:

- **Policy Framework:** Nigeria suffers from policy instability driven by high rate of turnover of programmes and personnel, which in turn has made the application of policy instruments unstable. The outcome is an uneven development pathway for agriculture; lack of policy accountability, transparency and due process of law, relating to willful violation of the constitution and subsidiary legislations governing the agriculture sector. This in turn has made the business environment unpredictable and discourages investors. To address this challenge, Nigeria needs to create a policy structure that matches evidence-driven coordination among decision-making authorities with common and public goals for an agricultural transformation of the country. Building that evidence base requires that Nigeria adopts a consistent fact base to drive decision making, as well as build on prior successes that is a continuity in policies in successive government. e.g. the Jonathan Administration's pioneering Agricultural Transformation Agenda (ATA).

- **Political Commitment:** This pertains to the non-implementation of international protocols or conventions agreed to with other members of the comity of nations. For example, Nigeria has failed to achieve the targets in the Maputo Declaration that prescribes a minimum of 10% budgetary allocation to the agricultural sector. Political commitment at both the Federal and State levels will be required to enforce reforms.

- **Agricultural Technology:** There is persistent shortcomings of the National Agricultural Research System (NARS) to generate and commercialize new agricultural technologies that meet local market needs. NARS's challenges have been relatively severe particularly around improved varieties of seed or other planting materials and breeds of livestock and aquatic species. The failure to also deliver already proven technologies available on the shelf to farmers' fields where they are needed is a challenge. Addressing these will require better coordination among extension delivery system, the national agricultural research system, as well as public and private sector suppliers of agricultural inputs.

- **Infrastructure Deficit:** Nigeria's agricultural sector suffers from an infrastructure challenge. Infrastructure such as motor roads, railroads or irrigation dams are either insufficient, or when available, not cost competitive. They are thus unable to operate to support scale-driven agriculture. That imposes an added cost (up to 50% - 100%) on the delivered price of agricultural produce in Nigeria, making it uncompetitive compared to global peers. In order to boost farm productivity, raise the level of marketable surplus and expand value chain participants' access to low cost infrastructure, Nigeria will need to rethink the business and operating model for agricultural infrastructure.

- **Finance and Risk Management:** Nigeria's agriculture sector continues to have poor access to financial services that enable farmers and other agricultural producers to adopt new technologies, improve market linkages, and increase their resilience to economic shocks. Poor access to financial services that enable input suppliers, processors, traders and others in agribusiness to address liquidity and encourage targeted private sector engagement in agriculture remains a challenge. Lending rates still routinely range from 10% to 30% subject to whether the borrower is considered prime, has access to low cost, government-provided financing (BoA, CBN, BOI), or is offered a NIRSAL Plc. -financed interest rate subsidy and credit guarantee. To improve financing options and de-risk value chains further, Nigeria will need to intensify innovation in financing ecosystems.

- **Institutional Reform and Realignment:** Today, many federal and state agricultural institutions only exist on paper. In fact, the system even ignores local government areas which is actually where a majority of activity takes place. There is a need to streamline, clarify mandates and ensure continued accountability for results. Unless these issues are tackled, Nigeria will continue to struggle with the capacity of its agricultural institutions to deliver on their public mandates. A turnaround will mean, for example, adding more resources such as adding up to 15,000 extension workers, setting up more operational coordination mechanisms between the Federal Government and States in between the National Council of Agriculture, and linking rewards to performance.

In addressing these constraints, the government will apply prudent, market based policy measures to grow the sector, with a clear recognition that widespread poverty reduction through the transformation of the agriculture sector is integral to the country's long run economic growth trajectory and prosperity. Accordingly, this policy statement is anchored on three main pillars in line with the constitutional provision for the role of Federal Government in agricultural development:

- Promotion of agricultural investment;
- Financing agricultural development programmes and
- Research for agricultural innovation and productivity.

AGRICULTURAL TRANSFORMATION AND DEVELOPMENT IN THE ECONOMY

Agricultural transformation is not only about food production, it is also about the development of the economy. FGN (2011) argues that economic development through agricultural transformation is achievable through the following four phases:

Import substitution agricultural development: Agricultural development with a focus on self-sufficiency via import substitution lowers the cost of food, increases real wages and drives down inflation.

Export-oriented agricultural sector: This involves a rapid transition to export-oriented agricultural policy that diversifies the economy and increase foreign exchange reserves as well as stabilizes the exchange rate. This policy will reduce inflation in the domestic economy and lead to macro-economic stability. Macro-economic stability will in turn significantly increase the level of foreign direct investment (FDI).

Growth value added agro-processing sector: Growth in foreign direct investment will lead to economies of scale derived from an export oriented large/efficient agricultural sector. This will provide inexpensive raw materials to stimulate investment in the agro-processing industry.

Backward integrate into higher value added manufacturing: With growth in agro-processing industry, backward integrate into higher value added services and manufacturing of industrial equipment and products for the burgeoning industry.

WAY FORWARD FOR EFFECTIVE AGRICULTURAL TRANSFORMATION IN NIGERIA

According to Federal Ministry of Agriculture and Rural development (FMARD) (2016), effective transformation of the agricultural sector is the only sure way to ensure food security and reduce hunger and mal-nutrition. To ensure this, the followings are recommended.

i. **Agriculture as a business** – focusing the policy instruments on a government-enabled, private sector-led engagement as the main growth driver of the sector. This essential principle was established in the ATA and will remain a cardinal design principle of Nigeria's agriculture policies going forward.

ii. **Agriculture as key to long-term economic growth and security—**focusing policy instruments to ensure that the commercialization of agriculture includes technologies, financial services, inputs supply chains, and market linkages that directly engage rural poor farmers because rural economic growth will play a critical role in the country's successful job creation, economic diversity, improved security and sustainable economic growth.

iii. **Food as a human right –** focusing the policy instruments for agricultural development on the social responsibility of government with respect to food security, social security and equity in the Nigerian society; and compelling the government to recognize, protect and fulfill the irreducible minimum degree of freedom of the people from hunger and malnutrition.

iv. **Value chain approach –** focusing the policy instruments for enterprise development across successive stages of the commodity value chains for the development of crop, livestock and fisheries sub-sectors, namely input supply, production, storage, processing/utilization, marketing and consumption. Building complex linkages between value chain stages will be an important part of the ecosystem that will drive sustained prosperity for all Nigerians.

v. **Prioritizing crops –** focusing policy on achieving improved domestic food security and boosting export earnings requires a measure of prioritization. Therefore, for domestic crops, the initial focus in 2016 – 2018 will be expanding the production of rice, wheat, maize, soya beans and tomatoes. For export crops, the initial focus will be on cocoa, cassava, oil palm, sesame and gum Arabic. In 2018 onwards, the export focus will add on bananas, avocado, mango, fish and cashew nuts. Investments in closing infrastructure gaps to accelerate productivity and investment in these crops will also be sequenced to reflect capital availability and management attention.

vi. **Market orientation –** focusing policy instruments on stimulating agricultural production on a sustainable basis, and stimulating supply and demand for agricultural produce by facilitating linkages between producers and off takers, while stabilizing prices or reducing price volatility for agricultural produce through market-led price stabilization mechanisms (commodity exchanges, negotiated off-take agreements, extended farm-gate price under value chains coordination mechanisms, agricultural insurance, etc.)

vii. **Factoring Climate change and Environmental sustainability –** focusing policy instruments on the sustainability of the use of natural resources (land and soil, water and ecosystems) with the future generation in mind while increasing agricultural production, marketing and other human activities in the agricultural sector.

viii. **Participation and inclusiveness –** focusing instruments on measures to maximize the full participation of stakeholders including farmer's associations, cooperatives and other groups, as well as NGOs, CBOs, CSOs, development partners and the private sector. This places a premium on the role of these organizations or groups as agents of economic change in general and agricultural economy in particular, thereby drawing benefits from their policy advocacy roles as partners to and watchdog of government.

ix. **Policy integrity –** focusing policy instruments on measures for sanitizing the business environment for agriculture, in terms of accountability, transparency and due process of law, ensuring efficient allocation and use of public funding and fighting corruption on all programmesinvolving public resources. This also applies to compliance with international commitments, protocols and conventions that Nigeria is a signatory to.

x. **Nutrition sensitive agriculture –** focusing policy instruments on addressing the issues of stunting, wasting, underweight and other manifestations of hunger and malnutrition with particular reference to the vulnerable groups, which include children under 5, nursing mothers and persons with chronic illness and disabilities.

xi. **Agriculture's Linkages with Other Sectors** – focusing policy instruments on the connected relationship between agriculture and other sectors at federal and state levels, particularly industry, environment, power, energy, works and water sectors.

Within this overall set of policy principles, the Federal Government will concentrate on providing an enabling environment for stakeholders at federal and state level to play their distinctive roles. The policy emphasis will be on providing a conducive legislative and agricultural knowledge framework, macro policies, security enhancing physical infrastructure and institutional mechanisms for coordination and enhancing access to adequate inputs, finance, information on innovation, agricultural services and markets.

Conclusion

The study examines the transformation of agricultural education and implication for food security in Nigeria. At independence in 1960, the level of hunger in Nigeria was minimal because majority of the people engaged in agriculture which they saw as means of sustenance. However, from 1970s when crude oil was discovered and subsequently exported, over 90% of government revenue came from crude oil export. This enables government to embark on a number of projects which injected much money into the economy. Consequently, agriculture was abandoned to the rural poor who continue to use crude implements. The result is food insecurity and hunger resulting in mal-nutrition in many homes. In order to transform the agricultural sector and ensure food security there must be adequate education especially on the use and application of agricultural tools and implements.

Recommendations

Having examined extensively the potentials of Nigerian agriculture sustainable development and the various factors that have hampered its growth over time, the following recommendations have emerged:

i. Government should focus development plan in agriculture and rural sector. A major policy reform that will set Nigeria in the path of agricultural transformation is for the government to make a conscious development efforts to revive the agricultural sector. In its urgent quest to diversify the economy due to the high volatility in the oil sector and recent economic recession in the land, agriculture should be made its priority. As Empirical studies in Nigeria has shown that agricultural growth is more pro poor than growth in non-agricultural sectors. Secondly, the huge agricultural potentials of the nation remains largely untapped. Thirdly, over 70 percent of the total Nigerian labour force is employed by the agricultural and rural sector. Therefore, focusing development efforts in agriculture and the rural sector will unleash positive development dividends for the nation.

ii. The Nigeria should enhance financing agricultural enterprises to unlock it's agricultural potentials.The federal government of Nigeria through its apex bank should reform and align its financial sector to increase their landing to agriculture. Some of the factors that led to the under-capitalization of the agricultural sector include high demands for collateral by banks; lack of capacity to develop appropriate credit instruments for agriculture and high interest rates. A recapitalization of the Nigerian Agricultural Cooperative & Rural Development Bank can further expand access to credit. It will also ensure longer term financing, with tenor of 5 years and above since commercial banks could not lend for long term needs of the agricultural sector.

iii. There should be Accelerate investment in agricultural infrastructure and marketing institutions. Given the low investment level in agricultural infrastructure in Nigeria, especially in the rural roads, most of the roads linking farmers to other sectors are inaccessible. Secondly, there is need to develop new and more efficient marketing corporations to replace the old marketing broads scrapped under the structural adjustment programmes of the World Bank and IMF. These institutions will help to improve the coordination of markets for agricultural commodities, provide market price information, improve access of farmers to credit and assure grades and standards. Developing market institutions and improved access to transport infrastructure will enable farmers get better market access and higher prices for their products. It will also encourage poor households mobility from subsistence production to off-farm jobs (DFD, 2015).

iv. There is need to create structural change in the labour composition of the Nigerian rural sector. Farm production alone is unlikely to provide the needed pathway out of poverty for the majority of the Nigerian rural poor. Apart from improving farm output through increased incentives to small holder subsistence farmers, achieving sustainable economic development in Nigeria will also require a private – public partnership in creating off-farm jobs or wage labour opportunities, in commercial agriculture, agro-based industries or the rural non-farm economy. Again, the federal government through its various agencies and ministries (such as DFRRI and NDE) should build linkages and promote greater mobility between rural and urban areas and/or between farm and non-farm opportunities.

v. There is need to develop appropriate technologies for and with the farmers who have not benefited from imported green revolution package of Asia and Latin America.

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Sorption Properties of Natural Rubber Filled With Chemically Treated Groundnut Shell Filler

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ABSTRACT

Sorption properties of natural rubber filled with chemically modified Groundnut shells were studied. Natural rubber composites were prepared using modified fillers at varying concentrations of sodium hydroxide (NaOH) Solution and acetylating solutions respectively. The processability conditions, sorption characteristics of these composites were analyzed. The fibre reinforcing efficiency of the chemically treated composites were compared with that of the untreated composite. The sorption properties of the composite also vary with the concentration of the mercerizing and acetylating agent. The improved properties observed were as a result of the increase in affinity between the rubber matrix and the chemically treated groundnut shell fillers.

Key words: Modified, Shell, Mercerization, Acetylation, Composite, Cross-linking, Sorption.

Introduction

Emergence of polymers in the beginning of the 19th century ushered a new era of research with a new option of using the natural fibres in more diversified fields. This renewed interest in the natural fibres has resulted in a large number of modifications to bring it at far and even superior to synthetic fillers. Because of such tremendous changes in the quality of natural fibres, they are fast emerging as a reinforcing material in composites (Rowell, 1998) considering the high performance standard of composite materials in terms of durability maintenance and cost effectiveness, applications of natural fibre reinforced composites as construction material in creating built environment holds the enormous potential and are critical for achieving sustainability. Fowler et al (2006) stated that materials from renewable resources are being sought as replacement and do not only act as reinforcement elements, but also the matrix phase of composite materials. It is not surprising, therefore, that more than 50% of all chemist, physicists, mechanical engineers and many material scientists are involved with research or development work with polymer composite. Rubbers as one of the classes of polymers have found great valued in many applications including engineering, sport, leisure and domestic. In its new state, rubbers may not be good enough for any useful application, so there is the need for the addition of additives which help to enhance the properties. Among these additives are fillers. Carbon black is the major filler used in rubber industry. Today there are lots of researches going on the use of an alternative (local source) for it (Ayo et al, 2011). Advances are being made into the use of agricultural by products, such as rice husk, dika-nut shell, etc in rubber composite (Ekebate et al, 2010). These materials are used in their raw form or they are modified before used. Groundnut shell is chosen because of its readily availability and also previous work has being done using ground shell by several research.

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Materials

The major materials required in this work are groundnut shell, natural rubber and the compounding ingredients. The preparation of treated groundnut shell powder, characterization of the filler, compounding, cure characteristics, vulcanization and the various tests carried out were carefully discussed as shown in Table 1.

Machines and Equipments

Tensile Properties

Machine: Instron Universal Tensometer, model: SSTM - Smart -1 - Series - 20KN, manufactured by Scientific Instrument Co. Ltd., U.S.A

Flexural Properties

Machine: Flex Tensometer, model: LCH - 150KN, manufactured by Vecomtech Co. Ltd., Viet Nam

Abrasion Resistance

Machine: Taber Oscillating Abrasion Tester, model: 6160 - F735, manufactured by Taber Co. Ltd., Canada

Compression Set

Machine: High Energy Compressor, model: CTM - 2P - 200 - 2000KN (200Tons), manufactured by Interlaken Technologies Co. Ltd., Thailand

Table - 1

Materials and their Sources

Materials	Sources
Natural Rubber	Famad Rubber Industry, Benin City
Groundnut Shells	Auchi, Edo State
Sodium hydroxide	British Drug House (BDH), England
Tetramethyl thiuram disulphide (TMTD)	British Drug House (BDH), England
Mercarpto benzothiazole sulphenamide (MBTS)	British Drug House (BDH), England
Stearic acid	British Drug House (BDH), England
Sulphur	British Drug House (BDH), England
Trimethylquinoline (TMQ)	British Drug House (BDH), England
Zinc Oxide	British Drug House (BDH), England
Processing Oil	British Drug House (BDH), England
Tetraoxo sulphate (Vi) acid	British Drug House (BDH), England
Acetic anhydride	Sigma Andriech, Germany
Glacial acetic acid	Sigma Andriech, Germany

Cure Characteristics

Machine: Mosanto Rheomter , model: MDR 2000 Series , manufactured by Interlaken Technologies Co. Ltd., Thailand

Fourier Transform Infrared Spectroscopy

Machine: Fourier Transform Infra-Red Spectrometer, model: Subpart ZZZZ-MACT-320, manufactured by Pine Equipments Co. Ltd., U.S.A

Hardness

Machine: Wallace Hardness Tester , model: c8007/25, manufactured by Interlaken Technologies Co. Ltd., Thailand

Method

Mercerization Process

Groundnut shells were pounded in a mortar to find particle size. After which, 40g each of were soaked in 5, 10,15, 20, 25, and 30% sodium hydroxide solutions for 1hour at room temperature. The solutions were then filtered ands thoroughly washed with distilled water, dry at room for 48 hours follow with oven drying at 110^{O}**C** for 2 hours.

Fibre – OH + NaOH -> Fibre – ONa + H_2O

Acetylation Process

Pounded groundnut shells were immersed in 20% sodium hydroxide solution for 1hour at room temperature. The alkaline treated shells were then soaded in 5% glacial acetic acid for 1hour at room temperature. The solutions were filtered and 40gs each of the filtered groundnut shell were soaked in 5, 10, 15, 20, 25 and 30%s acetic anhydride containing one drop of concentrated sulphuric acid for five minutes. The solutions were than filtered again and thoroughly washed with distilled water; try at room temperature for 48 hours follow with oven drying at 70^{o}C for 2 hours.

Fibre – OH + CH_3CO^- -> Fibre – $OOCH_3$ + H^+

Characterization of Filler

Fourier Transform Infrared Test

The Fourier Transform Infrared of the powdered samples will be carried out using the Fourier's Transform Infrared Spectrometer

Processing of the Composite

This involves Compounding of natural rubber with powdered groundnut shell filler. The formulation used for the compounding of the natural rubber (NSR 10) with the treated and untreated groundnut shell filler is given in Table 2.

Table 2

Formulation for Compounding Natural Rubber (Asore, 2000).

Ingredient	Parts per hundred rubber
Natural rubber	100
Fillers (GNS)	40
Zinc Oxide	5.0
Stearic acid	2.5
Sulphur	1.5
MBTS	1.5
TMTD	3.5
Processing Oil	5.0

A batch factor of seven was used to multiply the weight of the ingredients in parts per hundred of the rubber. After mixing, the rubber composite was stretched out. Mixing follow ASTMD 3184-80 standard

Mixing Procedure

The rubber mixes were prepared on a laboratory size two roll mill according to the mixing cycle shown in Table 3. It was maintained at 70^oC to avoid cross-linking during mixing after which the rubber composite was stretched out. Mixing follows ASTMD 3184–80 Standard.

Table 3
Mixing Steps and Mixing Time

Mixing steps	Time (minutes)
Natural rubber mastication	5
Addition of Stearic acid	1
Addition of Zinc Oxide	1
Addition of filler (GNS)	10
Addition of MBTS	1
Addition of TMTD	1
Processing Oil	1
Addition of Sulphur	2
Total	**22**

Cure Characteristics

The cure characteristics were determined using the Mosanto Rheometer, MDR 2000 model at 150^oC. The cure time predicted by the Mosanto rheographs was used as a guide to obtain vulcanizates for the test specimen.

Compounded Composite Curing

The curing of task pieces was done in a compression moulding machine. The curing was carried out at 140^oC for 15mins.

Mechanical Properties of the Composite

The mechanical properties of the composites formed were determined using standard task procedures.

Results

Results of the test carried out are shown in Tables 4 - 7:

Table 4
Swelling Behaviour of the Vulcanizates in Acetone

Sample Concentration (%)	Swelling Index (%)	Swelling Coefficient (%)	% mole uptake of the solvents
UT (0)	554	4.995	6.986
5	[346.40] (380.20)	[4.378] (4.806)	[5.963] (6.545)
10	[322.60] (354.10)	[4.079] (4.474)	[5.555] (6.096)
15	[286.00] (309.60)	[3.615] (3.909)	[4.923] (5.329)
20	[229.50] (246.00)	[2.900] (3.109)	[3.950] (4.236)
25	[278.20] (297.40)	[3.516] (3.760)	[4.789] (5.122)
30	[292.40] (323.80)	[3.696] (4.092)	[5.033] (5.574)

Key: Acetylated Vulcanizates [ ], Mercerized Vulcanizates ( )

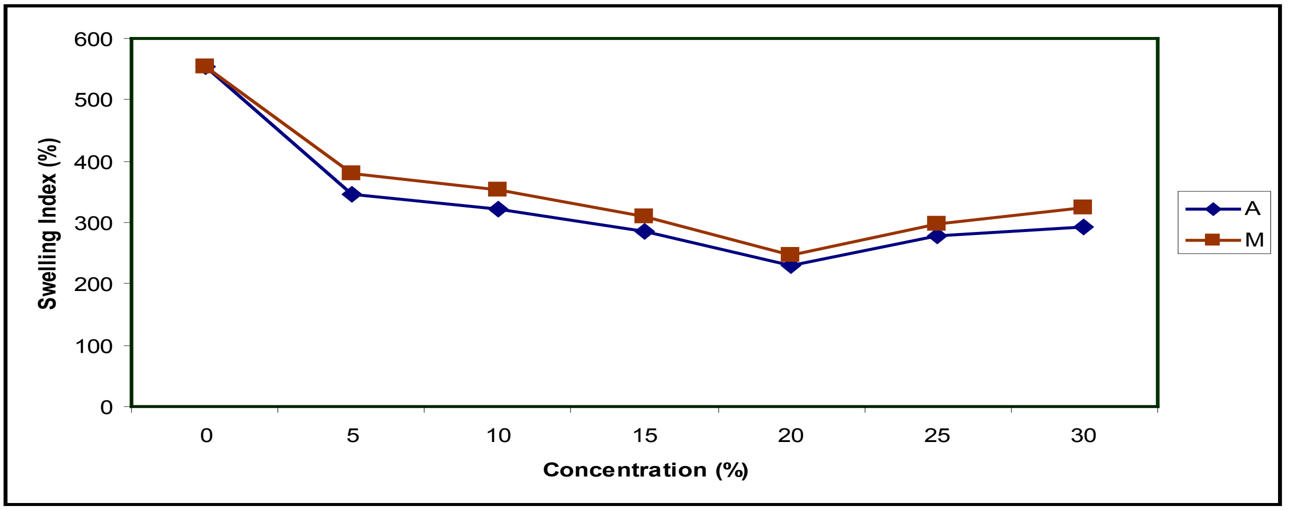

Figure 1: Swelling Index of the Vulcanizates in Acetone

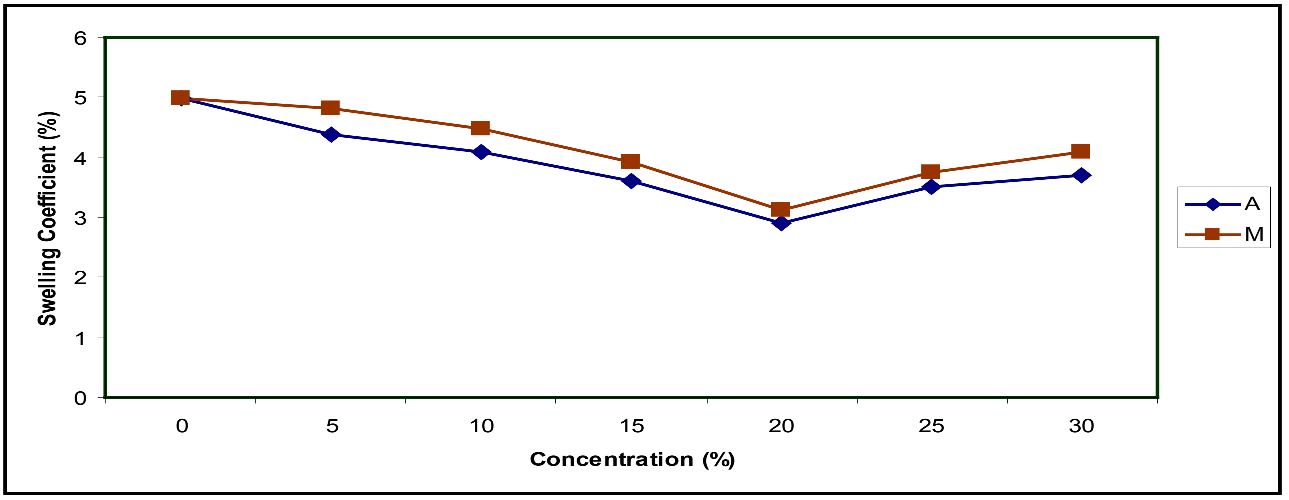

Figure 2: Swelling Coefficient of the Vulcanizates in Acetone

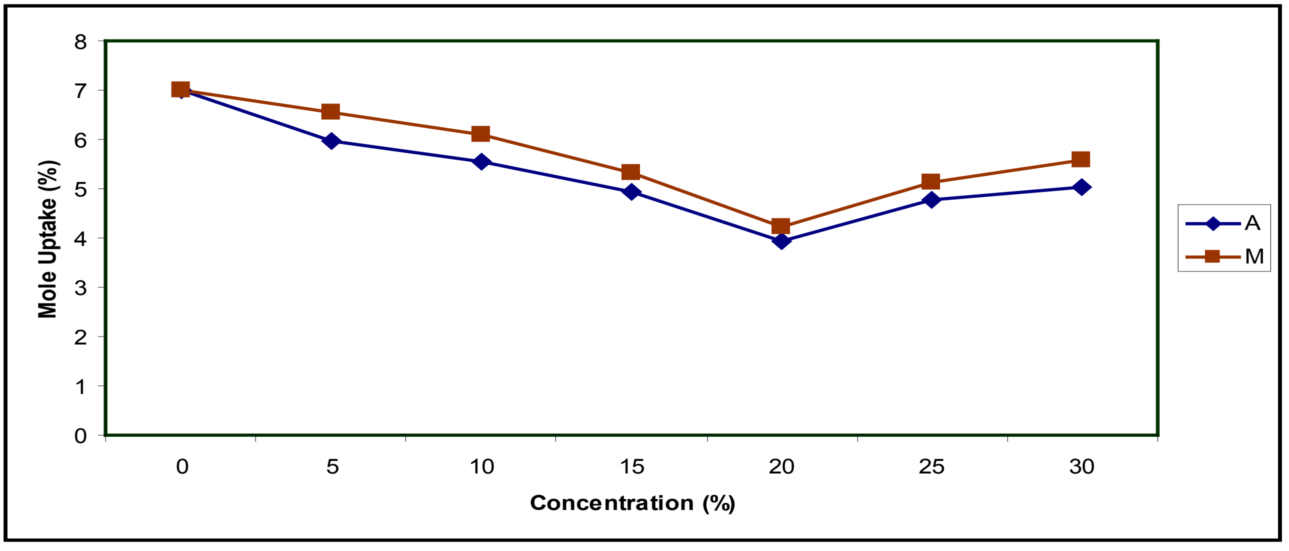

Figure 3: Mole Uptake of the Vulcanizates in Acetone

Table 5

Swelling Behaviour of the Vulcanizates in Xylene

Sample Concentration (%)	Swelling Index (%)	Swelling Coefficient (%)	Mole uptake of the solvents (%)
UT (0)	540	5.112	5.086
5	[384.00] (417.30)	[4.443] (4.848)	[3.616] (3.930)
10	[342.80] (408.60)	[3.967] (4.745)	[3.229] (3.848)
15	[300.20] (385.30)	[3.475] (4.476)	[2.828] (3.690)
20	[246.40] (342.00)	[2.852] (3.973)	[2.321] (3.221)
25	[308.50] (376.40)	[3.572] (4.371)	[2.907] (3.544)
30	[346.00] (380.00)	[4.005] (4.413)	[3.260] (3.578)

Key: Acetylated Vulcanizates [ ], Mercerized Vulcanizates ( )

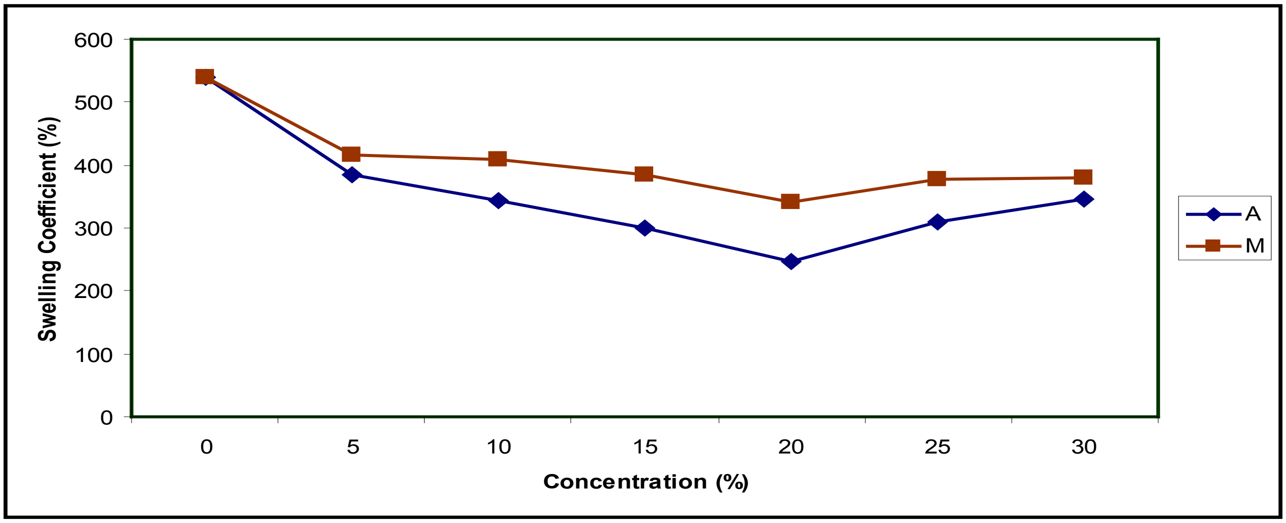

Figure 4: Swelling Index of the Vulcanizates in Xylene

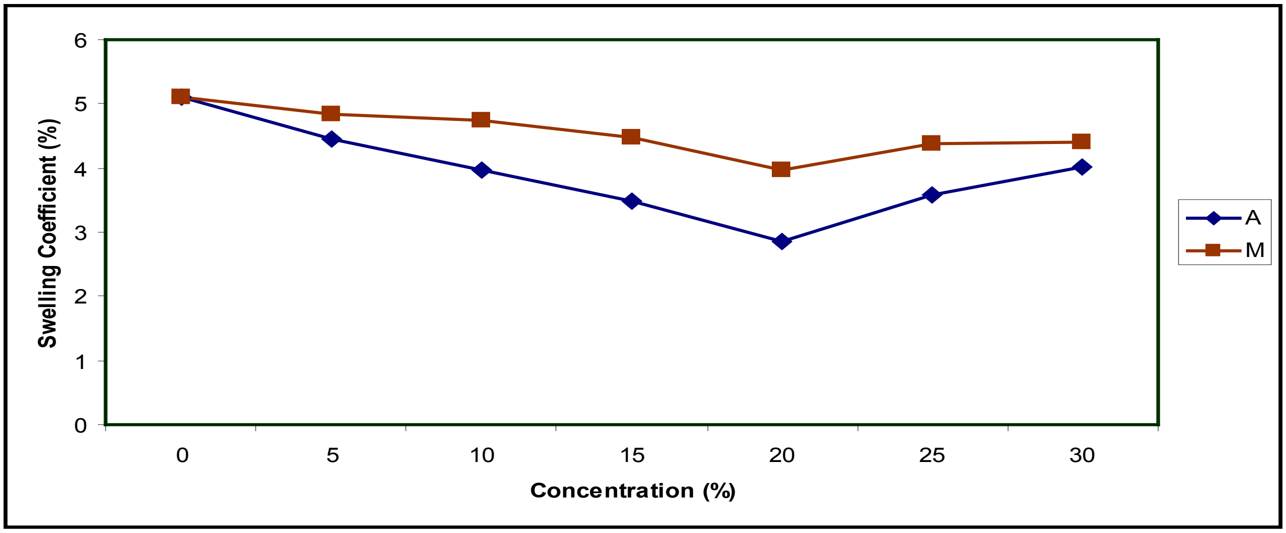

Figure 5: Swelling Coefficient of the Vulcanizates in Xylene

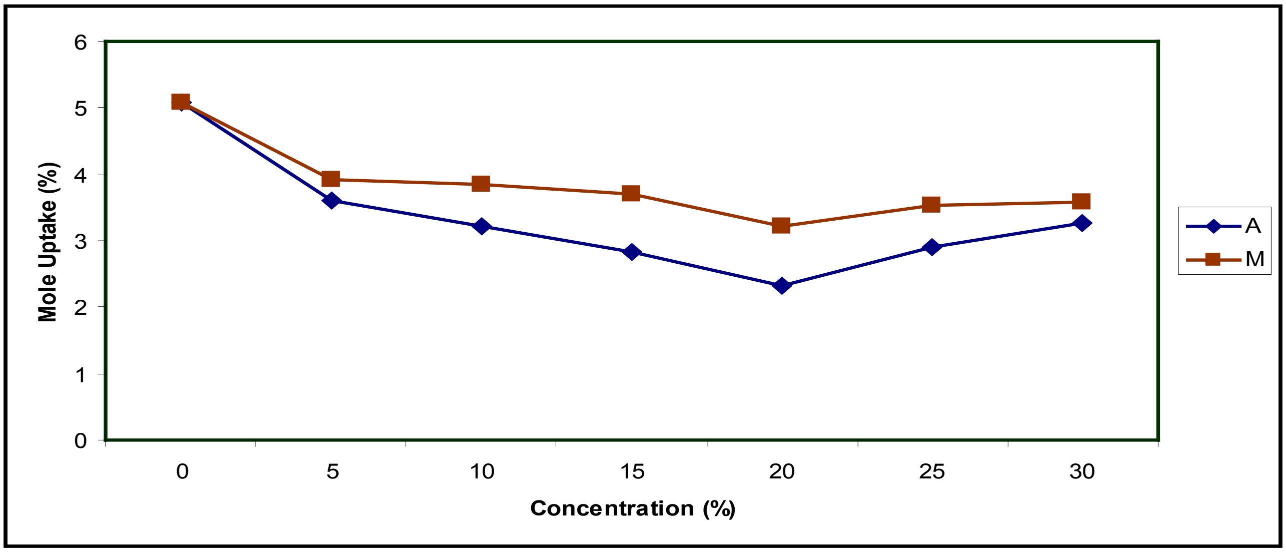

Figure 6: Mole Uptake of the Vulcanizates in Xylene

Table 6: Swelling Behaviour of the Vulcanizates in Toluene

Sample Concentration (%)	Swelling Index (%)	Swelling Coefficient	% mole uptake of the solvents
UT (0)	528.50	4.898	4.887
5	[368.20] (411.80)	[4.233] (4.750)	[3.997] (4.468)
10	[326.40] (400.60)	[3.753] (4.619)	[3.544] (4.347)
15	[294.00] (382.00)	[3.380] (4.406)	[3.191] (4.145)
20	[235.60] (365.40)	[2.709] (4.216)	[2.557] (3.966)
25	[296.90] (390.60)	[3.412] (4.506)	[3.221] (4.238)
30	[333.40] (391.20)	[3.833] (4.507)	[3.619] (4.240)

Key: Acetylated Vulcanizates [ ], Mercerized Vulcanizates ( )

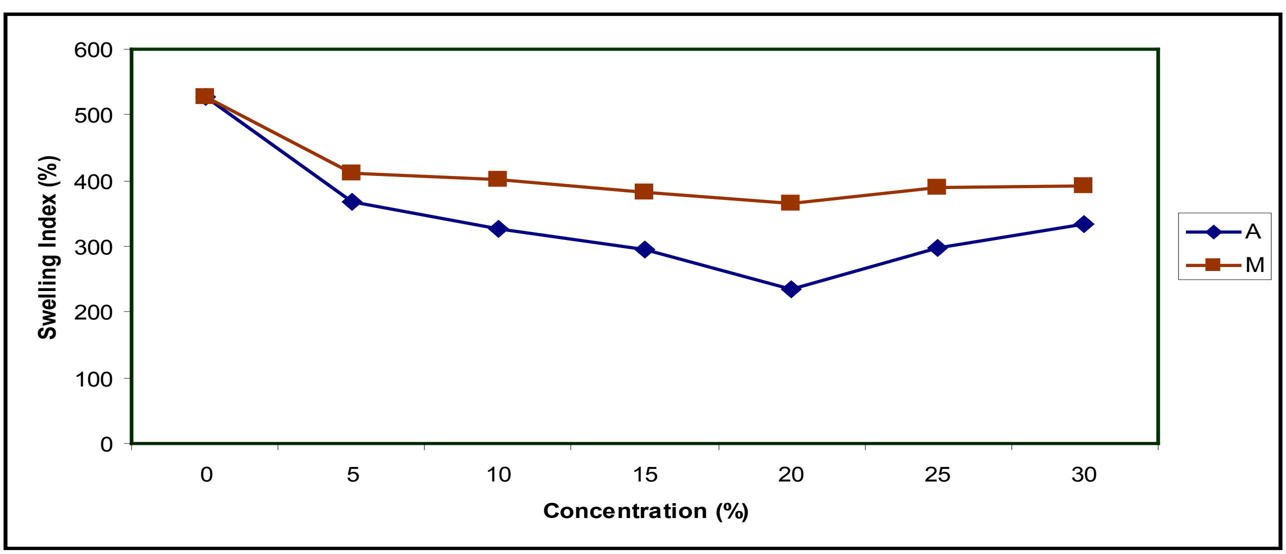

Figure 7: Swelling Index of the Vulcanizates in Toluene

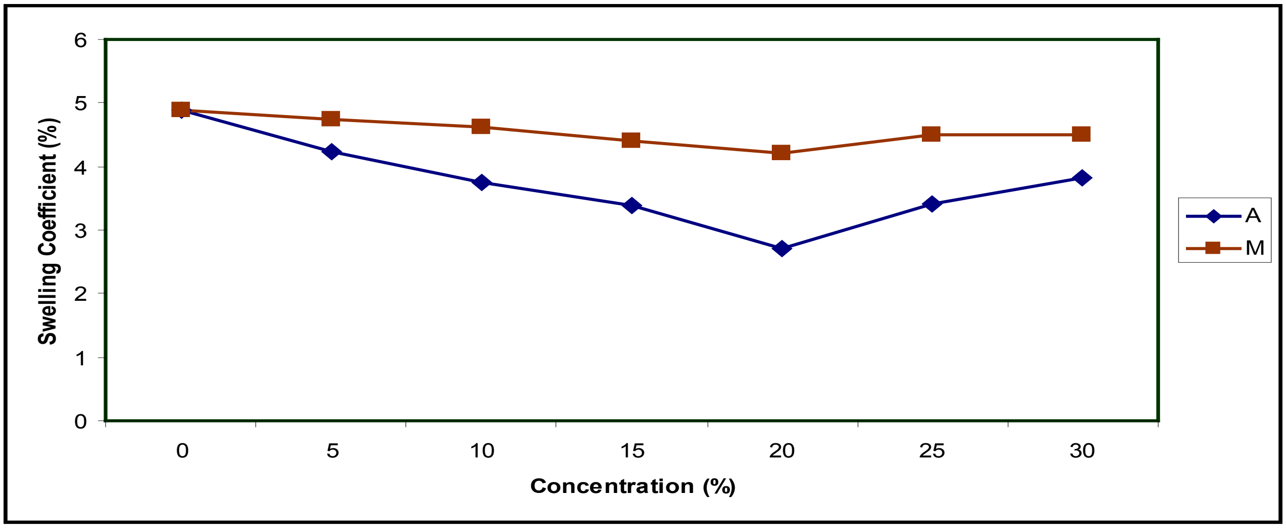

Figure 8: Swelling Coefficient of the Vulcanizates in Toluene

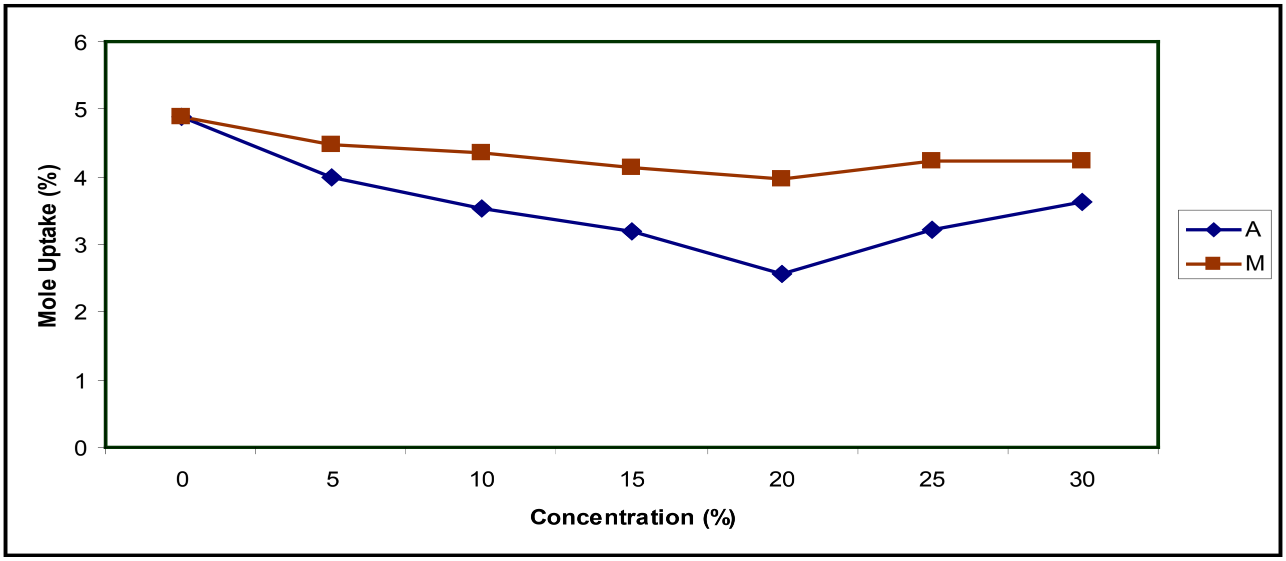

Figure 9: Mole Uptake of the Vulcanizates in Toluene

Table 7:
Cross-linking Density of the Vulcanizates

Sample	Cross-linking Density (Kg/cm)
5	(15.50) [20.04]
10	(23.48) [28.06]
15	(20.33) [24.08]
20	(22.96) [41.08]
25	(15.37) [28.42]
30	(11.88) [23.54]
UT	19.21

Key: Acetylated vulcanizates [ ], Mercerized vulcanizates ( )

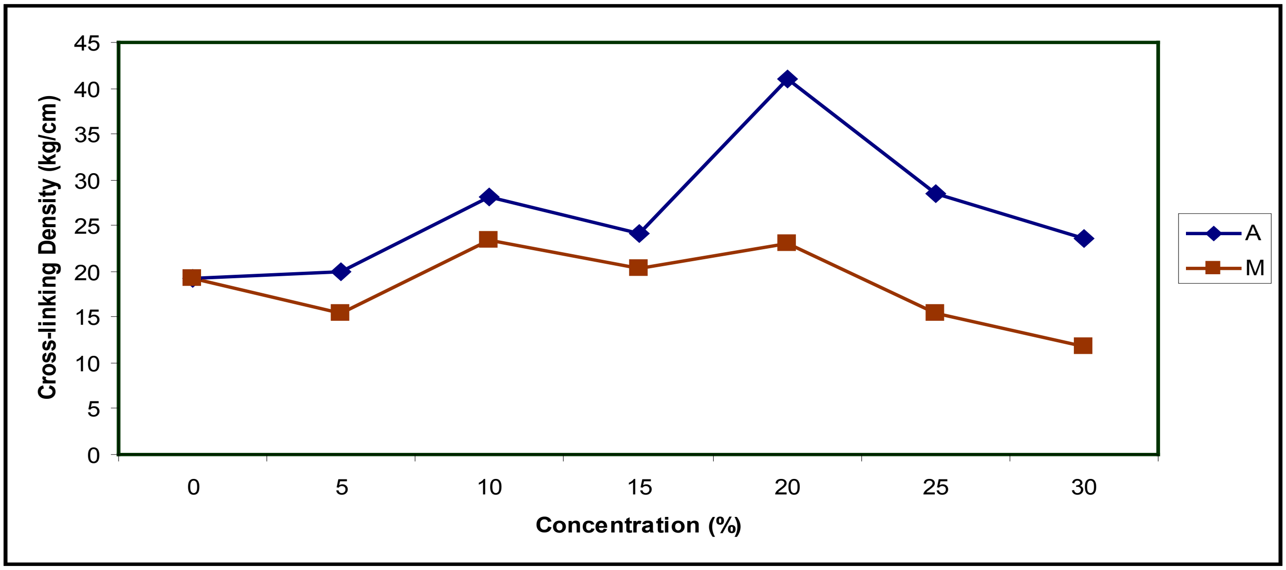

Figure 10: Cross-linking Density of the Vulcanizates

Discussion

The results of the sorption behaviour of the vulcanizates presented in Table 4.7 - 4.10 show the influence of chemical treatments. In the entire composite samples, it was observed that the mole percentage uptake of the solvents decreases with increase in concentration of the acetylating and mercerizing agents (Ahmedna et al, 1997). This shows that chemical treatments increases the interfacial adhesion between rubber and fibres and thus increase the cross-link density. This prevents entry of the solvents. The acetylated fibres show better results than the mercerized fibres which is in agreement with previous work by Ekebafe et al (2011). The results presented show highest percentage swelling for acetone for both acetylated filler-filled and mercerized filler-filled vulcanizates. This is expected because the solubility parameter of acetone is closest to natural rubber than other solvents used in this research work. The solubility parameter of the relevant solvents used include; acetone (9.77 $(cal/cm^3)^{0.5}$), Xylene (8.85 $(cal/cm^3)^{0.5}$) and toluene (8.91 $(cal/cm^3)^{0.5}$) (Wang, 2004). In all the relevant solvents used the percentage swelling of the vulcanizates decreases with chemical treatments of the fibres (Bledzki et al, 1999). The swelling index percentage also follows the same trend. The diffusion mechanism in rubbers is essentially connected with the ability of the polymer to provide pathways for the solvent to progress in the form of randomly generated voids (Kalia et al, 2009). As the voids formation decreases with the addition of fibres, the solvent uptake also decreases (Ekebafe, et al, 2011). The densities of the solvents used in this research work are as follows; toluene (0.870g/ml), acetone (0.791g/ml) and xylene (0.864g/ml) respectively.

Conclusion

Most of the chemical treatment from literature reviewed indicates decrease in the strength properties at high concentration levels because of the disintegration of the non-cellulosics materials. Mercerization and acetylation studied from this communication shows that at low concentration, treatment lead to strong covalent bond formation, increase fibre matrix adhesion and thereby enhancing the composite strength (Saira et al, 2007). It also shown that groundnut shell is a potential substitute for glass fibres, based on the fact that chemical treatment of groundnut shell have achieved some degree of success in making a superior interface, mechanical properties and sorption behaviour. The preliminary results of the assessment revealed that groundnut shell is hydrophilic due to the presence of the hydroxyl group from cellulose and lignin. Chemical treatment reduces the hydrophilicity of the fibre by decreasing the hydroxyl groups in the fibres.

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A Comparative Study of Physicochemical Properties of Freeze-dried Camel's Milk and Cow's Milk Powder

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ABSTRACT

In the present study, fresh raw camel and cow's milk were concentrated to 20-30% total solids, and then freeze-dried under the temperature of (-50 °C to -75 °C), under vacuum. The physicochemical characteristics of the various freeze-dried powders were determined. The water activity (aw) of freeze-dried camel milk (FDC) and freeze-dried cow milk (FDW) ranged 0.253-0.307 and 0.148- 0.301, respectively. While aw of the commercial milk sample (CMD) was 0.326. Both FDC and FDW had reasonable flowability as indicated by measuring their hausner ratio which ranged between 1.15 and 1.24. FDC had higher insolubility index (0.65-0.85) when compared with those of FDW(0.25-.055). The yield and hygroscobisity of freeze-dried samples ranged between (81.42-94.57) and 22.12-27.32, respectively. The measurements for colour characteristics indicated that the lightness ranged between 91.20 and 94.34 while the commercial sample had a value of 94.45. All samples had acceptable lightness, yellowness and redness when compared with those of the commercial sample. Small variation were determined in some of the chemical components of the various samples of FDC, FDC and CMD. It is recommended in the present investigation that freeze-drying of milk could be an extremely effective method for producing dried powder from camel and cow's milk with little changes in most nutrient compounds

***Keywords*:** Freeze drying, water activity, flow-ability, acidity, concentration, protein.

INTRODUCTION

The dromedary camel, otherwise called the Arabian camel, exists today only as a domesticated animal. About 90 percent of the world's camels are dromedaries. There are two types of Bactrian camels: wild and domesticated. A camel can go possibly more than seven days without water, and it can last for several months without food. It can survive a 40 percent weight loss and then drink up to 32 gallons (145 liters) of water in one drinking session [1].

Camel milk is an important source of proteins for the people living in the arid lands of the world. Camel milk is also known for its medicinal properties, which are widely exploited for human health, as in several countries from the ex-Soviet Union and developing countries[2-4].

Camel milk and camel milk products have dependably been exceedingly regarded playing even today an imperative part in the diet of the population in the rustic zones of Africa, Asia and the Middle East, with rare agricultural areas, high temperatures and small amount of precipitation. The camel delivers in the vicinity of 1000 and 2000 L of milk during the lactation period of 8 to 18 months, while the daily production of milk is in the vicinity of 3 and 10 L [5]. Camel milk products in the world are popular due to increasing demand and are typically available in pharmacies [6].

Cow milk seems to be everywhere, and is regularly underestimated, however it has numerous essential medical advantages for people, including its ability capacity to help in weight reduction, assemble strong bones and teeth, support the immune system, reduce fat, protect the heart, prevent diabetes, eliminate inflammation, and help stimulate growth. There were variations in constituents of camel's milk than in cow's milk. The main difference between cows and camels milk lies in the different physicochemical characteristic of the individual components[7].

Lyophilization (freeze drying) is a procedure in small amounts of a product will be frozen, then placed under

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vacuum. Through vacuum the frozen liquid sublimates and ice immediately changes to vapour, without to defrost. After that the water is removed closer and closer till the core of the product. The lyophilization process is considered as an excellent drying process for heat sensitive products Regardless of the advantages, it is notable that the process has been perceived as the most costly process for manufacturing a dehydrated product [8-11]. Hereby the structure of the product stays intact and that's why the dried product can absorb quickly after the process. Due to the vacuum the ice will evaporate immediately without turning in to water again, and this ensures that most of the taste, of the surface and of the supplements will remain in place [12]. Reasonable parameters of process application enable us to obtain best quality products compared to products dried with customary techniques[13]. The objectives of the present study were to produce freeze dried camel milk with acceptable color and flow ability and to compare the physicochemical and functional properties of freeze dried camel's milk and cow's milk powder..

MATERIALS AND METHODS

Materials

Raw camel's milk and cow's milk were supplied by Al Ain Dairy Company. In addition, commercial cow milk powder samples were bought from a local supermarket in Alain, United Arab Emirates to be used in the study.

The freeze–drying process

Hundred ml raw camel's milk were cow's milk, were placed in especially glass bottles for freeze-drying, then glass containers was placed in were the deep freezer under a temperature of -75 °C for 24 hours, then the glass bottles placed in a freeze-drying, under the temperature of (-50 °C to -75 °C), under vacuum, to obtain the Freeze-dried powder.

Determination of physicochemical properties

The physicochemical properties of camel milk were determined as follows: Water activities of freeze dried powders were determined using a water activity analyzer (Rotronic SW with hydrolyte VD sensor, Rotronic Instrument Corp., Huntington, NY). The flowability (Hausner ratio) is the ratio of un-tapped bulk density and tapped bulk density. Un-tapped bulk density was determined by sifting milk powder into a 100 ml cylinder and then weighing. Tapped bulk density was determined by reading the volume after tapping the cylinder 100 times [14].

For determination of solubility (amount of a substance that can be dissolved in a given amount of solvent),10 g of whole milk powder was mixed with 100 ml of water at approx.. 24 °C in mixer at high speed for 90s.The milk then was left for 15 min. After which it was stirred with a spatula. 50ml was filled into a graduated 50 ml centrifuge glass. The glass was spun in a centrifuge for 5 min, the sediment free liquid was sucked off, the glass was filled up again with water and the content was stirred up. Then the glass was placed into the centrifuge and spun for 5 min after which the sediment was read. The sediment was expressed in ml and was termed insolubility index. It usually below 0.2 ml in powder from good quality milk dried in designed dryers.

Process yield was calculated as the relation between total solids content in the resulting powder and total solids content in the feed mixture. Hygroscopicity values (determined by moisture gain by 2 g of powder samples) were measured under saturation solution of $Na2SO4$. After 1 week, hygroscopic moisture was expressed as g of moisture per100 g dry solids (g/100g) to determine hygroscopicity.

Hygroscopicity (g/100g) = (Wf – Wi)X100)/(Wi X(100-moisture/100) Where: Wf = final weight . Wi = initial weight.

Colour determination

The color of different samples was measured using a colorimeter (Hunter lab).The results were expressed in the CIE L, a, b. which determined the degree of lightness, redness and yellowness characteristics of the various milk powder samples Where L = is an indication of lightness. A = is an indication of redness. B = is an indication of yellowness.

Chemical analyses

The contents of moisture, ash, protein, total soluble solids, fat and titratable acidity were determined according to AOAC[15] methods. The pH value was determined using a pH meter (model HANNA pH 211 micro processor) according to AOAC[15] method. The ascorbic acid (vitaminC) content was determined in spray dried milk powder samples according to the AOAC [16].

RESULTS AND DISCUSSION

Physicochemical properties

Physicochemical properties of the various samples is presented in Table (1). The water activity (aw) of freeze-dried camel milk (FDC) and freeze-dried cow milk (FDW) ranged 0.253-0.307 and 0.148- 0.301, respectively. While aw of the commercial milk sample (CDM) was 0.326. It seems that the concentration, temperature, direction of feed and type of milk did not affect water activity of freeze dried samples but it gave different results for commercial sample.

Data in Table (1) show the untapped bulk density of different of freeze-dried camel's milk, freeze-dried cow milk and commercial dried milk. The Freeze drying produced powder with lighter un-tapped bulk density (0.38-0.52) as compared to commercial sample (0.37).These values were relatively lower than those tapped bulk density which ranged between 0.29-0.45 compared to that of commercial milk which was 0.30.

The hausner (flowability) ratio of freeze-dried camel's milk and freeze-dried cow's milk ranged 1.15-1.31 and 1.13-1.28, while the hausner ratio for the commercial milk was 1.23. All these values fall within the standard value for free

Table- 1

Physicochemical properties of Freeze-dried camel milk (FDC), Freeze-dried cow's milk (FDW) and commercial milk (CDM).

Run No.	aw	Untapped bulk density	Tapped bulk density	Haunser ratio	Insolubility Index	Yield	Hygroco-picity
FDC 1	0.307	0.52	0.45	1.15	0.85	91.23	27.32
FDC 2	0.334	0.38	0.29	1..31	0.85	81.42	26.23
FDC 3	0.253	0.41	0.33	1.24	0.65	94.57	26.72
FDW1	0.148	0.38	0.31	1.22	0.45	90.24	22.81
FDW2	0.326	0.42	0.37	1.13	0.55	91.23	22.12
FDW3	0.301	0.45	0.35	1.28	0.25	92.5	24.13
CDM	0326	0.37	0.30	1.23	0.10	ND	18.23

powder flowing , indicating the efficiency of freeze drying of both camel milk and cow's milk of acceptable flowability as indicted by De Jong et al.[17] who stated that A hausner ratio of 1 to 1.25 indication the powder had free flowing, hausner ratio of 1.25 to 1.4 indicate fairly free flowing powder, and powder with hausner ratios greater than 1.4 are cohesive and do not flow well.

The freeze–dried camel's milk powder had higher insolubility index (0.65-0.85) when compared with those of freeze-dried cow's milk (0.25-.055).The commercial had less insolubility index freeze-dried samples, this may be due to additions of some materials to facilitate the solubility. The degree extent to which milk powders are insoluble in water has generally been measured in the milk powder industry using an insolubility test (solubility index, SI), basically developed by the American Dry Milk Institute [18] and adopted by the International Dairy Federation [19]. The yield (the actual amount of substance obtained during preparation of a substance) of freeze-dried camel milk and freeze-dried cow milk powder raged 81.42 -94.57 and 90.24-92.5, respectively.

Hygroscopicity is is the ability of a substance to attract water molecules from the surrounding environment through either absorption or adsorption [20]. The data in Table (1) show the hygroscopicity of different freeze-dried camel's milk, freeze-dried cow's milk and commercial milk. It was found that the hygoscopicity of different powder milk was not affected by type of milk.Never the less, the freeze-dried milk powder samples had more hygroscopicity (22.32 to 27.32) than that of the commercial sample (18.23), and also more than the range determined by Suliemanet. al. [20] for spray-dried camel milk and cow milk powder (20.43 to 20.47).

Colour characteristics of freeze-dried milk powder

Generally many parameters are used in judging the colour of dried milk powder. These parameters include:

i- L value which is an indication of lightness and blackness. If the l is 100 the color is white. If the l is 0 the color is black.

ii- A value is an indication of redness and greenness. If the a value is positive, it indicates redness, if a value is negative, it indicates greenness.

iii- B value is an indication of yellowness and blueness. If the B value is positive, it indicated yellowness, if B value is negative, it indicated blueness.

Table- 2

Lightness of different milk powder samples

Run No	Lightness	Redness	Yellowness
FDC1	94.34	-2.28	11.09
FDC2	92.84	-0.73	10.75
FDC3	91.20	-2.36	12.98
FDW1	93.49	-0.10	15.20
FDW2	94.16	-0.14	13.42
FDW3	92.84	-0.10	14.21
CMD	94.45	-0.28	21.84

Data in Table (2) show the colour characteristics of freeze-dried milk powder made from camel and cow's milk. The lightness ranged between 91.20 and 94.34 while the commercial sample had a value of 94.45. These results indicate that although slight changes observed in the various samples, however, the lightness of all samples were acceptable. As for the redness, freeze-dried samples from both types of milk had valuesranging between -0.1 and -2.28 so indicated greenness. The yellowness ranged between 10.75 and 12.98 for the freeze-dried camel milk, while the freeze-dried cow milk had relatively higher values (13.42-15.20) and the commercial milk which was 21.84. It has been stated that the drying temperature affect the yellowness, low temperature produced less yellowness in comparison to high temperature [20].

The colourchanges of freeze dried milk powders could be bought about by Millard reactions, lipid peroxidation, degradation of ascorbic acid or sugar-sugar caramelisation,as suggested by Davies and Labuza [21] who attributed colour changes in milk powder to non-enzymatic browning reactions.

Chemical characteristics

It is realized that changing of environment significantly affects regular physiological function of both human and animals, so it was essential to analyze camel and cow milk powder on Sudanese environment. The chemical composition of freeze-dried camel's milk (FDC), freeze-dried cow milk (FDW) and commercial milk (CMD) is presented in Table (3). The moisture content of FDC (2.44 -3.0%) were relatively greater than those of FDW (1.43-1.87%), while the commercial milk had a moisture content of 1.7%. However, the fat content ranged between 21.88 and 29.24%, was not affected by concentration and type of milk, but it should be noted that cow milk naturally contains more fat than camel milk, and this explains the relatively higher fat contents of FDW when compared with those of FDC samples.

The protein contents of FDC of FDW ranged between 23.54-25.30% and 22.61-25.02%, respectively. However, protein content of CMD was 25.42%. The ash contents of the various freeze- dried samples ranged between 5.78and 8.05% which fall within the range of CMD which was 5.44%. Increase in the ash content of camel's milk was due to its large amount of minerals and vitamins, as compared with milk cow, therefore, FDC exceeded FDW samples in their ash contents. The titrable acidity (expressed as lactic acid%) of FDC of FDW ranged between 0.162-0.205% and 0.155-1.75%, respectively. However, the titrable acidity of CMD was 0.155%. Generally, the acidity of milk is affected by concentration and type of milk [22].

Changes in the composition of some constituents in freeze-dried milk can be clarified as a function of the freeze-dried process. These progressions harmonized with changes in moisture content [23].

Table - 3
Chemical composition of Freeze-dried camel milk (FDC), Freeze-dried cow's milk (FDW) and commercial milk (CDM)

Run No.	Moisture %	Fat %	Protein %	Ash %	Titrable Acidity %
FDC1	3.00	21.25	25.30	7.78	0.162
FDC2	2.44	22.96	24.35	8.05	0.205
FDC3	2.64	22.46	23.54	7.46	0.191
FDW1	1.43	22.88	22.61	6.96	0.175
FDW2	1.87	23.18	26.28	5.94	0.173
FDW3	1.82	29.24	25.02	5.44	0.155
CMD	1.70	31.89	25.42	5.28	0.155

FDC:Freeze-dried Camel's milk, FDW: Freeze-dried cow's milk,CMD :commercial cow'ssamples.

CONCLUSIONS

Based on the results of the present study, it is concluded that freeze-drying of camel and cow's milk could be an efficient method for producing acceptable products with little changes in most nutrient compounds. The flowability of all camel's milk and cow's milk powder were within the recommended values 50°C thus promoting a fairly good flow.It is recommended to pack dried products is vacuum, in order to obtain products with better functional and physicochemical properties.

Further investigations are required to approve the possibilities of camel milk powder on an industrial scale and to encourage utilization of camel's milk powder as sustenance fixings in snacks, chocolates, ice cream, infant formulae.

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Spectroscopic and Thermodynamic Properties of 3-Phenyl-4-(3-Methoxybenzylidenamino)-4,5-Dihydro-1H-1,2,4-Triazol-5-One Compound

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ABSTRACT

In this study, 3-phenyl-4-(3-methoxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one was synthesized by the reaction of 3-phenyl-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-one with 3-methoxy-benzaldehyde. The molecule was optimized by using B3LYP/6-31G(d) HF/6-31G(d) basis sets. ^{1}H-NMR and ^{13}C-NMR spectral data values were calculated according to the method of GIAO using the program package Gaussian G09W. Experimental and theoretical values were inserted into the graphic according to equitation of δ exp=a+b. δ calc. The standard error values were found via SigmaPlot program with regression coefficient of a and b constants. Also, calculated IR data of compound were calculated in gas phase by using of 631G(d) basis sets of B3LYP and HF methods and are multiplied with appropriate adjustment factors. Theoretical infrared spectrums are formed from the data obtained according to B3LYP method. In the identification of calculated IR data was used the veda4f program. Furthermore, molecule's theoretical bond lengths, UV-Vis values, dipole moments, mulliken charges, HOMO-LUMO energies, total energy of the molecule for both methods were calculated. Experimental data were obtained from the literature.

Key words: 1,2,4-triazol-5-one, GIAO, B3LYP, HF, 6-31G(d).

Introduction

The optimized molecular structure, vibrational frequencies, UV–Vis spectroscopic parameters, atomic charges and frontier molecule orbitals (HOMO and LUMO) of the titled compound have been calculated by using DFT/B3LYP and HF method with 6-31G(d) basis set. All quantum chemical calculations were carried out by using Gaussian 09W [1, 2] program package and the GaussView molecular visualization program [3]. The molecular structure and vibrational calculations of the molecule was computed by using Becke-3-Lee Yang Parr (B3LYP) [4, 5] density functional method with 6-31G(d) basis set in ground state. IR absorption frequencies of analyzed molecule were calculated by two methods. Then, they were compared with experimental data, which are shown to be accurate. Infrared spectrum was composed by using the data obtained from both methods [6, 7]. The assignments of fundamental vibrational modes of the title molecule were performed on the basis of total energy distribution (TED) analysis by using VEDA 4f program [8]. In this study, 3-phenyl-4-(3-methoxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one was synthesized by the reaction of 3-pheny

l-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-one with 3-methoxy- benzaldehyde [9].

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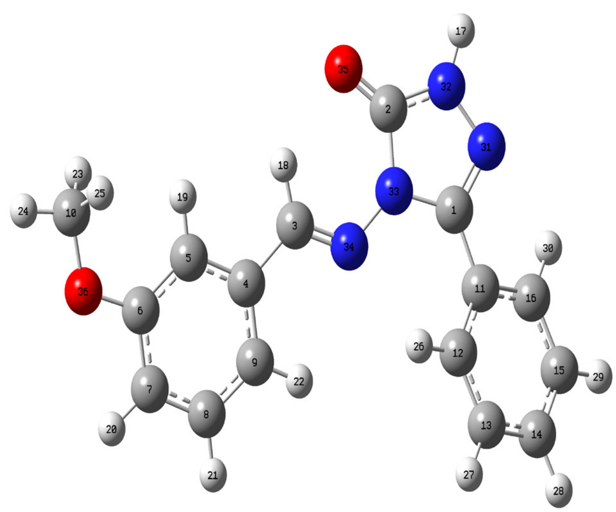


Figure 1. The optimized molecular structure of 3-phenyl-4-(3-methoxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one with DFT/HF 6–31G(d) level.

Methods

The molecular structure of the title compound in the ground state (in vacuo) is computed by performing both Hartree-Fock (HF) and the density functional theory (DFT) by a hydrid functional B3LYP functional (Becke's three parameter hybrid functional using the LYP correlation functional) methods [1, 2] at 6-31G(d) level. In all these theoretical calculations, the basic or stimulated state of molecules or atoms can be used [1, 10]. The geometric optimizations of all structures can be generated by the MM2 method and then the semi-empirical PM3 method [11].

Results and Findings

Molecular Structure

The optimized molecular geometric parameters (bond lengths and bond angles) of the molecule by using B3LYP/6–31G(d) and HF/6–31G(d) levels are listed in Table 1 and 2.

Table 1

The calculated bond lengths of the molecule

Bond Lengths (°)	HF	B3LYP	Bond Angles (°)	HF	B3LYP
C1-C11	1,4703	1,47030	C9-H22	1,0844	1,08440
C1-N31	1,3071	1,30710	C10-H23	1,098	1,09800
C1-N33	1,3968	1,39680	C10-H24	1,0914	1,09140
C2-N32	1,3699	1,36990	C10-H25	1,098	1,09800
C2-N33	1,419	1,41900	C10-O36	1,4194	1,41940
C2-O35	1,2229	1,22290	C11-C12	1,4041	1,40410
C3-C4	1,4667	1,46670	C11-C16	1,4059	1,40590
C3-H18	1,0878	1,08780	C12-C13	1,3944	1,39440
C3-N34	1,2892	1,28920	C12-H26	1,0824	1,08240
C4-C5	1,4069	1,40690	C13-C14	1,3954	1,39540
C4-C9	1,4024	1,40240	C13-H27	1,0866	1,08660
C5-C6	1,3977	1,39770	C14-C15	1,3971	1,39710
C5-H19	1,0846	1,08460	C14-H28	1,0867	1,08670
C6-C7	1,4023	1,40230	C15-C16	1,3916	1,39160
C6-O36	1,3643	1,36430	C15-H29	1,0866	1,08660
C7-C8	1,3928	1,39280	C16-H30	1,0849	1,08490
C7-H20	1,0855	1,08550	H17-N32	1,0083	1,00830
C8-C9	1,3935	1,39350	N31-N32	1,3734	1,37340
C8-H21	1,0867	1,08670	N33-N34	1,3736	1,37360

Table 2

The calculated bond angles of the molecule

Bond Angles	HF(°)	B3LYP(°)	Bond Angles	HF (°)	B3LYP (°)
C11-C1-N31	122,4587	122,45870	H24-C10-H25	109,2692	109,26920
C11-C1-N33	126,8029	126,80290	H24-C10-O36	105,8651	105,86510
N31-C1-N33	110,7363	110,73630	H25-C10-O36	111,5804	111,58040
N32-C2-N33	101,3828	101,38280	C1-C11-C12	122,9501	122,95010
N32-C2-O35	129,6062	129,60620	C1-C11-C16	117,8498	117,84980
N33-C2-O35	129,0091	129,00910	C12-C11-C16	119,1475	119,14750
C4-C3-H18	117,8127	117,81270	C11-C12-C13	120,0631	120,06310

C4-C3-N34	120,0463	120,04630	C11-C12-H26	119,8723	119,87230
H18-C3-N34	122,1401	122,14010	C13-C12-H26	120,0646	120,06460
C3-C4-C5	117,5622	117,56220	C12-C13-C14	120,5067	120,50670
C3-C4-C9	122,5206	122,52060	C12-C13-H27	119,4012	119,40120
C5-C4-C9	119,9171	119,91710	C14-C13-H27	120,0915	120,09150
C4-C5-C6	120,1436	120,14360	C13-C14-C15	119,6621	119,66210
C4-C5-H19	118,9174	118,91740	C13-C14-H28	120,1767	120,17670
C6-C5-H19	120,939	120,93900	C15-C14-H28	120,1613	120,16130
C5-C6-C7	119,6614	119,66140	C14-C15-C16	120,1915	120,19150
C5-C6-O36	124,6154	124,61540	C14-C15-H29	120,1796	120,17960
C7-C6-O36	115,7231	115,72310	C16-C15-H29	119,6278	119,62780
C6-C7-C8	119,9377	119,93770	C11-C16-C15	120,4283	120,42830
C6-C7-H20	118,5123	118,51230	C11-C16-H30	118,9673	118,96730
C8-C7-H20	121,5497	121,54970	C15-C16-H30	120,6044	120,60440
C7-C8-C9	120,8963	120,89630	C1-N31-N32	105,0303	105,03030
C7-C8-21	119,3013	119,30130	C2-N32-H17	125,0605	125,06050
C9-C8-21	119,8021	119,80210	C2-N32-N31	114,5613	114,56130
C4-C9-C8	119,443	119,44300	H17-N32-N31	120,2173	120,21730
C4-C9-H22	119,44	119,44000	C1-N33-C2	108,2707	108,27070
C8-C9-H22	121,1154	121,11540	C1-N33-N34	122,3996	122,39960
H23-C10-H24	109,277	109,27700	C2-N33-N34	128,8527	128,85270
H23-C10-H25	109,1661	109,16610	C3-N34-N33	119,0781	119,07810
H23-C10-O36	111,5996	111,59960	C6-O36-C10	118,3532	118,35320

Vibrational frequencies

The 3-phenyl-4-(3-methoxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one have 36 atoms and the number of the normal vibrations is 102. The observed and calculated vibrational frequencies, the calculated IR intensities and assignments of vibrational frequencies for title compound are summarized in Table 3.

Table 3

The calculated frequencies values of the molecule

	Vibration types	B3LYP	HF
1	τ NCNN, τ CCCC, τ NNCC	16	13
2	τ NCCC, τ NCNN, τ CNNC	29	23
3	τ NCCC, τ NCNN, τ CCCC	49	48
4	δ NNC, τ NCNN, τ CCCC,	58	60
5	δ NCC, δ CCC, δ NNC	66	67
6	τ CCCC, τ CNNC	74	72
7	δ CNN, δ NCN, τ CNNC	93	86
8	τ NCNN, τ CCCC, τ CNNC	102	98
9	τ HCCN, τ CNNC	148	155
10	τ NNCC, τ CCCC	152	163

11	τ CNNC, τ NNCC	160	171
12	δ CNN, δ NCN, δ CCC	182	177
13	τ NCCC, τ CCCC	197	183
14	δ CNN, δ NCN,	212	206
15	ν CC, δ CNN	215	216
16	τ CCCC, τ NNCC,	249	234
17	τ NNCC, τ CCCC	268	252
18	τ NCNN, τ NNCC, τ CCCC	276	265
19	τ HNNC, τ CNNC	286	282
20	τ NNCC, τ CCCC	297	291
21	ν CC, δ CNN, τ CNNC	324	296
22	δ CCC, δ CCN	336	297
23	δ CCC, τ OCCC	348	320
24	τ HOCC	353	339
25	δ CNN, δ OCN, δ OCC, δ NNC	376	382
26	τ CCCC, τ NNCC, τ OCCC	395	405
27	τ HCCC, τ CCCC	416	422
28	δ OCC, δ CCC, τ OCCC	434	430
29	δ OCN, δ OCC, δ CCC	436	439
30	τ HNNC, τ ONNC	444	440
31	ν NC, δ CNN, τ ONNC	469	471
32	δ CNN, τ ONNC	516	502
33	δ CCC, τ HCCC, τ CCCC	523	524
34	δ CCC, τ OCCC	523	537
35	τ HCCC, τ CCCC, τ OCCC	544	552
36	δ OCN, δ CNN, δ CCN	579	588
37	δ CNN, δ CCN	604	602
38	ν CC, δ NCN	611	611
39	ν CC, δ NCN, τ CNNC	625	623
40	δ CCC	635	637
41	δ NNC, τ HCCN	638	642
42	τ HNNC, τ NNCC, τ CNNC	642	659
43	τ HCCC, τ CCCC	686	697
44	τ HCCC, τ CCCC, τ OCCC	708	721
45	δ CCC, τ OCCC	712	736
46	τ ONNC	722	751
47	ν CC, ν NN, δ CCC	749	775
48	ν NN, δ CCC	766	789
49	ν NC, δ CNN	783	794
50	τ HCCC	792	814

51	τ OCCC, τ HCCC	803	821
52	ν CC, ν OC	808	826
53	τ HCCC, τ OCCC	818	848
54	ν CC, δ NCC, δ NNC	863	865
55	τ HCCC, τ CCCC	926	965
56	δ NNC, τ HCCN	934	977
57	τ HCCC, τ CCCC	942	988
58	δ HCH, δ NNC, τ HCCN	963	993
59	τ HCCN	989	997
60	δ CCC, δ HCC	993	1036
61	δ HCC, τ HCCN	1020	1042
62	δ HCH, τ HCCN	1035	1056
63	ν NC, ν NN, δ NNC	1037	1069
64	ν NN, δ HNN, τ HCCN	1069	1078
65	ν CC, δ HNN, τ HCCN	1076	1094
66	ν CC, δ HCC,	1091	1103
67	ν CC, δ HCC	1149	1119
68	δ HOC, δ HCC	1159	1156
69	ν NC, ν NN	1168	1190
70	ν CC	1211	1226
71	ν NN, δ NCN	1246	1230
72	ν OC, ν NN, δ NCN	1255	1233
73	ν CC, ν OC	1259	1268
74	ν CC, δ HCC, δ HOC	1292	1313
75	ν CC, δ HOC, δ HCC	1329	1325
76	ν NC, δ HCH, δ HCN	1339	1369
77	δ HNN, δ HCH	1351	1395
78	δ HCH, δ HCN	1378	1405
79	δ HCH, δ HCN	1391	1416
80	ν NC, δ HCH, δ HCN	1408	1427
81	ν CC, δ HCC	1423	1442
82	δ HCH, τ HCCN	1425	1442
83	δ HCH, τ HCCN	1444	1467
84	ν CC, δ HCC	1501	1525
85	ν CC	1571	1606
86	ν NC, ν CC, δ HCC	1591	1630
87	ν NC, ν CC	1601	1690
88	ν NC, ν CC	1617	1709
89	ν NC	1724	1702
90	ν OC, ν NC	1748	1771

91	ν CH	2908	2848
92	ν CH	2950	2893
93	ν CH	2978	2916
94	ν CH	3002	2950
95	ν CH	3043	2981
96	ν CH	3051	3000
97	ν CH	3052	3014
98	ν CH	3064	3026
99	ν CH	3071	3035
100	ν CH	3098	3044
101	ν CH	3101	3050
102	ν NH	3767	3761

ν, stretching; δ, bending; δs, scissoring; ρ, rocking; γ, out-of-plane bending; τ, torsion

NMR spectral analysis

In nuclear magnetic resonance (NMR) spectroscopy, the isotropic chemical shift analysis allows us to identify relative ionic species and to calculate reliable magnetic properties which provide the accurate predictions of molecular geometries [12-14]. In this framework, the optimized molecular geometry of the molecule was obtained by using B3LYP and HF methods with 6–31G(d) basis level in DMSO solvent. By considering the optimized molecular geometry of the title compound the ^{1}H and ^{13}C NMR chemical shift values were calculated at the same level by using Gauge-Independent Atomic Orbital (GIAO) method. Theoretically and experimentally values [9] were plotted according to δ exp=a. δ calc.+ b, Eq. a and b constants regression coefficients with a standard error values were found using the SigmaPlot program.

Table 4

The calculated and experimental ^{13}C and ^{1}H NMR isotropic chemical shifts of the molecule

No	Exper.	DFT/631d/DMSO	Diff./DMSO	HF/631d/DMSO	Diff/DMSO
C1		150,90	-150,90	146,40	-146,40
C2		153,05	-153,05	146,57	-146,57
C3		156,49	-156,49	150,27	-150,27
C4		139,59	-139,59	131,65	-131,65
C5		119,52	-119,52	110,47	-110,47
C6		161,70	-161,70	152,36	-152,36
C7		124,35	-124,35	116,42	-116,42
C8		133,39	-133,39	127,97	-127,97
C9		120,52	-120,52	112,97	-112,97
C10		62,78	-62,78	47,02	-47,02
C11		131,07	-131,07	121,91	-121,91
C12		133,64	-133,64	128,81	-128,81
C13		131,94	-131,94	123,54	-123,54
C14		134,07	-134,07	129,29	-129,29

C15		132,37	-132,37	124,23	-124,23
C16		132,21	-132,21	127,49	-127,49
H17	12,20	7,74	4,46	6,90	5,30
H18	9,54	10,25	-0,71	9,66	-0,12
H19	6,87	7,05	-0,18	6,87	0,00
H20	6,95	7,24	-0,29	7,02	-0,07
H21	7,30	7,75	-0,45	7,53	-0,23
H22	7,70	8,09	-0,39	7,68	0,02
H23	3,82	4,15	-0,33	3,36	0,46
H24	3,82	4,16	-0,34	3,39	0,43
H25	3,82	4,46	-0,64	3,84	-0,02
H26	7,88	8,51	-0,63	8,01	-0,13
H27	7,60	7,94	-0,34	7,65	-0,05
H28	7,65	7,95	-0,30	7,81	-0,16
H29	7,55	7,92	-0,37	7,64	-0,09
H30	7,80	8,33	-0,53	8,04	-0,24

Table 5

Mulliken atomic charges of the molecule

	HF	**B3LYP**		**HF**	**B3LYP**		**HF**	**B3LYP**
C	0,3952	0,2969	**C**	-0,1003	-0,0782	**H**	0,1195	0,1334
C	0,6763	0,4774	**C**	-0,0111	-0,0115	**H**	0,1040	0,1160
C	0,2533	0,0917	**C**	-0,1762	-0,2568	**H**	0,1043	0,1200
C	-0,1574	-0,0792	**C**	-0,1910	-0,2564	**H**	0,1288	0,1389
C	-0,0131	-0,0362	**H**	0,2596	0,2493	**H**	0,1153	0,1284
C	-0,0785	-0,0511	**H**	0,1202	0,1211	**H**	0,1282	0,1319
C	0,2748	0,1625	**H**	0,1270	0,1163	**N**	-0,3752	-0,3038
C	-0,1023	-0,0738	**H**	0,1232	0,1186	**N**	-0,2833	-0,2236
C	-0,0583	-0,0756	**H**	0,1139	0,1065	**N**	-0,4835	-0,3741
C	0,6917	0,4533	**H**	0,1019	0,0972	**N**	-0,2680	-0,1753
C	-0,3114	-0,2390	**H**	0,1254	0,1122	**O**	-0,5007	-0,3640
C	-0,0073	-0,0213	**H**	0,0955	0,0927	**O**	-0,5201	-0,3609
C	-0,0990	-0,0779	**H**	0,0939	0,0917	**O**	-0,4377	-0,3227
C	-0,0958	-0,0844	**H**	0,1184	0,1098			

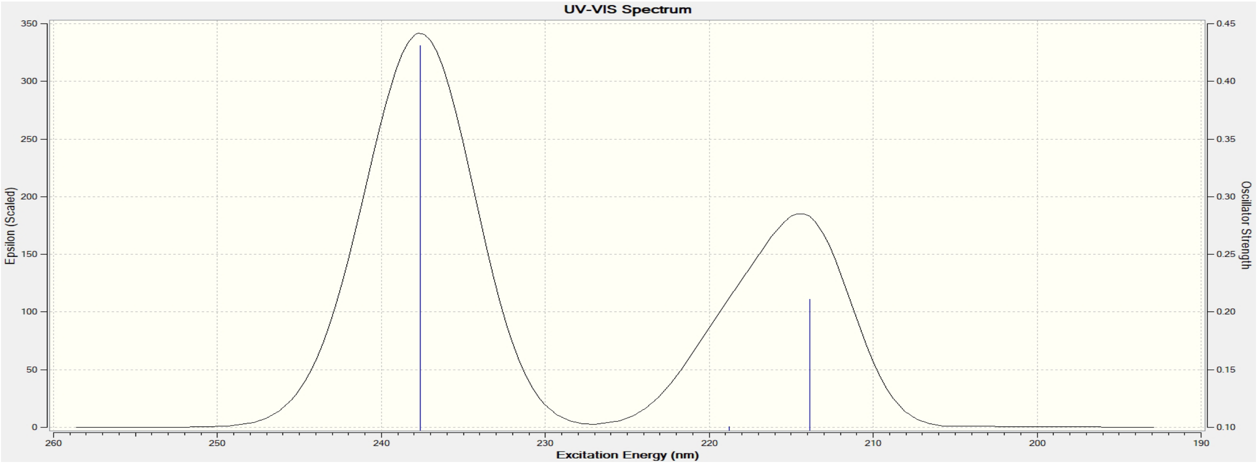


Figure 2. UV spectra simulated with B3LYP/6–31G(d) levels of the molecule.

Table 6
The experimental and calculated absorption wavelength (λ), excitation energies and oscillator strengths (f) of the molecule

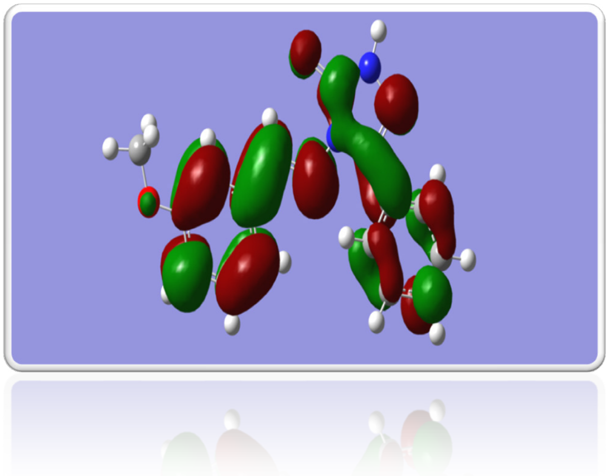
λ (nm)	Excited State (eV)	f (oscillator strengths)
B3LYP	**B3LYP**	**B3LYP**
237.64	5.2174	**0.4312**
218.80	5.6664	**0.1005**
213.85	**5.7977**	**0.2109**

Table 7
The total energy of the of titled compound

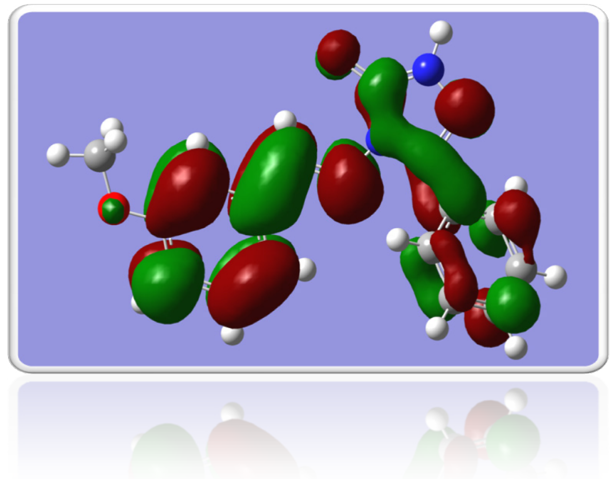
Energy	B3LYP	HF
a.u.	-987,546	-981,522

Table 8
The calculated dipole moment values of the molecule

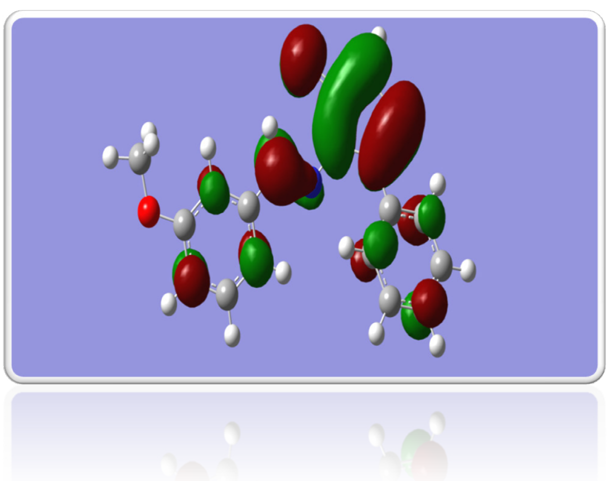
Dipole Moment	B3LYP (a.u.)	HF (a.u.)
μ_x	-0.4111	-0.1049
μ_y	-0.6156	-1.3012
μ_z	0.3039	0.3349
μ_{Toplam}	0.8002	1.3477



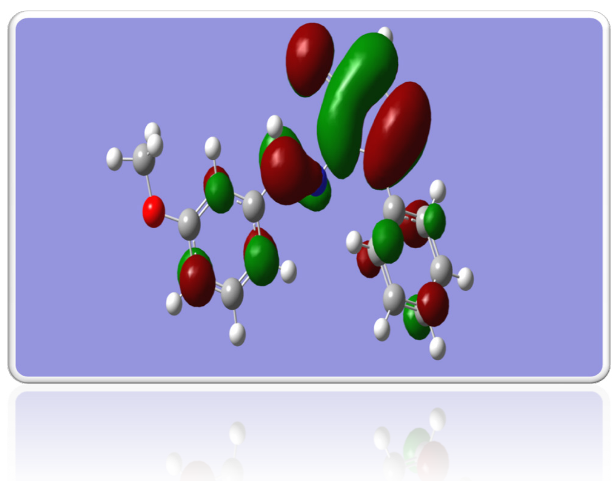
E_{LUMO} (B3LYP) : -0,18898 Hatree



E_{LUMO} (B3LYP) : -0,18668 Hatree



E_{HOMO} (B3LYP) : -0,28151 Hatree



E_{HOMO} (B3LYP) : -0,28861 Hatree

Figure 3. The calculated HOMO-LUMO energies of the molecule according to DFT/B3LYP/6–31G(d) and HF/B3LYP/6–31G(d) levels

Conclusion

The molecular structures, vibrational frequencies, ^{1}H and ^{13}C NMR chemicals shifts, UV–vis spectroscopies, HOMO and LUMO analyses and atomic charges of 3-phenyl-4-(3-methoxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one molecule synthesized for the first time have been calculated by using DFT/B3LYP and HF methods. By considering the results of experimental works, it can be easily stated that the vibrational frequencies, ^{13}C and ^{1}H NMR chemical shifts and UV spectroscopic parameters obtained theoretically are in a very good agreement with the experimental data.

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