

Competitive Bidding – Research and Development - 2007

Programs in Competency of Grantor

Program

The Environment and Conservation of Natural Resources

Code of Program

Project of a New Alternative Technology Approach of Liquid Hydrocarbons Production Suitable for Combustion Engines on the Base of Natural Inexhaustible and Renewable Resources.

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Research Period: 2009 - 2010

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Object of Industry: Trade Certificate – Building Contractors

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B. Proposal for Procedure and Solution of the Project

B.1. Target of the Project

B.1.0. Annotation of Author

I deal with this idea approximately from January 2007. Idea is based on real possibility to connect two different chemical reactions into just one reaction performance by using of selective catalysts under the conditions to operate finally all this potential technological process continuously. The mere idea is essentially very simple and easy so that maybe by this reason technology conception which is presented at the end of this syllabus can evoke in some of readers uncertain feelings. Very important notice is that it is just approximation of future potential and perhaps even pursuable and meaningful technology which meanwhile doesn't exist in the world. Basically conception of all project is only consequence of **chemical and technology mind experiment** and that's why I would be very grateful to readers for their patience and tolerance in reading of the following text. In this way presented conception of whole project is in a matter of fact becoming pure proposal for serious and rigorously performed basic scientific research with possibility to extend it into sphere of possible technological improvement, of course on the ground that this basic scientific research will be accomplished successfully. In fine I would like to thank readers very much for understanding and patience in reading of this imperfect translation of original from Czech language into English.

Author of the project: Mr. Magister. Martin Skoda

B.1.1. Preface

Target of this project is **building** of dynamic and **fully automated continuously working pilot plant** for production of **liquid hydrocarbon fraction approximately about C15 – C19 carbon atoms in aliphatic chain**, suitable for using into contemporary combustion motors. Base material for this pilot plant will be **vegetable oil and animal oil and fat**. Project has got two **user-oriented** parts:

- 1st part focuses on vegetable oil coming from primary agricultural sector (especially.rape oil under european conditions)
- 2nd part focuses on waste, used eventually superfluous fats and oils coming from secondary sectors (processing industry – animal fats from rendering plant ,waste cooking oil from catering industry etc..)

Both of these user-oriented parts of research project will realize concurrently. Built up pilot plant will become just **model – starting point** for the purpose of economic, environmental and safety criteria of performance monitoring. This monitoring should take at least one callendar year. If this model will come true all rigorous criteria of EU after performance of monitoring then all project will be regarded as terminated. Next eventual questions of potential industrial building of a big plant will not be a subject of this project. Although this project in term of final projection falls into the field of **organic technology**, nevertheless with its complex survey project covers a **basic scientific research** in the field of **organic chemistry**.

The sense of this research project is to contribute at least in part for solving worldwide and global crisis in problems of crude-oil production and its actual and prevalent way of exploitation. This crisis is already coming and it's evident that it will deepen very fast in horizon of the next 20 – 30 years.

Sense of exhaustibility of this very valuable and herewith nonrenewable natural resource is generally extended around all the world indeed however existing way of the final processing and exploitation of crude-oil fractions for particular branch of industry does not correspond to this knowledge and this categorical imperative of nature is still underestimated.

Project is based on philosophy of connection of high environmental needs with economic aspects. Anyway, exploitation of crude-oil fractions for fuel production and energetic industry is not just worldwide profusion but first of all it's one-way carbon dioxide emission into earth's atmosphere and consequently also hazard of greenhouse effect and global warming increasing. Crude oil is extremely valuable source of big amount of very various basic organic compounds which are already prepared before and ready above all for chemical and pharmaceutical industry not for energetics and motorism. Project has as one's task by means of a small but very well qualified and cooperating team to facilitate to bridge the economic and environmental gap between challenge of nature and essential human need to use vehicles increasingly.

B.1.2. Alternative Fuels in Light of Nowadays

In the late 20th and at the beginning of 21st century human population uses these following alternative fuels for combustion engines that are originally different from fuels on the base of fossil sources. Of course, crude oil as the most important fossil resource in this matter is still not fully fungible by raw and really recent and renewable alternative fuels therefore in the majority of the cases there is necessity to mix fossil and recent sources of fuels together. At least at the present days. Despite of fact natural gas is also already used as alternative fuel in modified spark ignition engines of some of companies (Fiat Multipla Natural Power, Mercedes-Benz NGT Sprinter etc) [Department of Physical Chemistry](#) problems of natural gas as alternative motor fuel is not discussed in this work because it is just fossil resource of energy.

Dimethyl Ether (DME)

DME is gaseous fuel. It's possible to produce it both from natural gas and from living mass as well. As motor fuel DME is used in the form of condensed gas which requires using of unique and technically mature fuel feed system. Conveniences: Low level of emissions of greenhouse gases, low emission of dangerous substances for the human health. Disadvantages: In term of short-period forecast DME production requires investment into infrastructure very similar to that of infrastructure for Liquefied Petroleum Gas (LPG)

Methanol and Bioethanol

Bioethanol is produced by fermentation from crop-plants that are rich in sugar and starch (farina). It is regarded as fuel with the biggest potential in term of short-period forecast. Methanol is produced by catalytic process from hydrogen enriched synthesis gas. It's possible to mix ethanol and methanol with diesel oil in a different proportion and to obtain approximately the same energetic content. Conveniences: It was evident ascertained by deep analysis for Swedish highway administration that the first candidate for petrol replacement is methanol produced from forest scrap. Methanol can be also useful in term of long-period forecast because it works without any adjustment in some types of fuel clusters. Disadvantages: Methanol is very harmful for human health and it is necessary to manipulate it under the special conditions – totally hermetic systems. Some volume of ethanol production comes from Sweden however this amount is not satisfactory and ethanol fuel is imported in particular from Brazil at the present days.

Manure Gas (Biogas)

The main component of biogas is methane produced by biological decomposable materials or by means of biomass gasification. Biogas is produced by anaerobic bacterial fermentation from biologically decomposable material. Sources of biogas are: equipments for waste-water treatment, food-processing industry and processing of sorted household refuse. It can be obtained by biomass gasification as well. Unfortunately manure gas is suitable just for petrol engines: Conveniences: This process doesn't generate any additional carbon dioxide and even particulate and nitrogen oxides emissions are lower than at the same car model using diesel oil instead. If gasification of biomass is productional method then all biogas manufacturing process produces very low emission of greenhouse gases. Disadvantages:

Biogas needs extensive, expensive and exacting car modification and high investment into a new infrastructure. This infrastructure is of the same kind like infrastructure for processing of natural gas.

Biogas plus Gaseous Hydrogen

Gaseous Hydrogen can be produced by gasification of biomass or water electrolysis. Its normal concentration in biogas is about 8% but higher concentration is also possible. Conveniences: View to environment. Disadvantages: Very high investments are needed for massive constructional car modification and for infrastructure as well. This infrastructure is the most expensive of all.

Synthetic Motor Oil (Petroleum)

Synthetic oil is a mixture of hydrocarbons obtained by chemical procedure - gasification of renewable living mass. This technology is still in stage of research and development. Synthetic oil is suitable for Diesel motors without necessity to make any constructional changes or a new adjustment. This fuel can be mixed with classic motor oil in any proportion. Also for storage and distribution it's possible to use present and existing infrastructure. Conveniences: Synthetic oil embodies very low carbon dioxide emission within all cycle of its usage. Disadvantages: Although synthetic oil can be produced from grown crop-plants, forestry refuse or from other biological materials its effect and influence during combustion process is lower than for example in the case of DME, methanol or biogas. Investment costs for its production are high and therefore there is a big risk of expensiveness of the final fuel after delivery to fuel filling stations. But again - this technology approach is still only in stage of research and development at the present days.

Biogas plus Synthetic Motor Oil / Biogas plus Biodiesel

Both of these combinations embody very similar economic effects. Biogas can be combined with biodiesel (Fatty Acids Methyl Esters) ev. with synthetic motor oil by using of separated tanks and injection valve systems. In this case biogas must be cooled and maintained in liquid condition. There must be about 10% of biodiesel ev. synthetic oil injected first inside of Diesel motor for attainment of sufficient compression and flash. Conveniences: Combustion process runs without any decrease in power of Diesel motor. Same the cars using biogas as fuel have got higher force and they are more reliable than the cars using natural gas. By virtue of manure gas this fuel option protects environment very well and has got the big potential for the future. The biggest advantage is that for biogas production it's possible to use refuse material or sewerage water. Disadvantages: One of disadvantages is that biogas under liquid condition is approximately about 25 % more expensive than compressed biogas. Next – in the case of biogas and biodiesel it's necessary to invest funds into infrastructure. The reason is a low stability of biogas and biodiesel during storage.

Molecular Hydrogen

Molecular hydrogen is already discussed as a potential alternative fuel for the distant future and then it's not actual in term of short-period forecast of development. Using of hydrogen as alternative fuel of the future requires massive constructional adjustments of petrol engines and high investment into new infrastructure.

Vegetable Oil

Vegetable oil can be also used in the specially re-built and adjusted Diesel motors. The biggest disadvantage is that vegetable oil can break through to mineral lubricant motor oil (infiltration) and with time to start to polymerize there. As a result motor can be seriously damaged in the end.

Biodiesel

Natural source for production of biodiesel is mostly vegetable oil coming from primary agricultural sector eventually from secondary sector of industry as well. Common oils are following: rape oil, sunflower oil, palm-oil and soybean oil. It's possible to use also oil descended from exotic plants. The most common secondary source is waste cooking oil coming from catering industry. Biodiesel is chemically mixture of **fatty acids methyl esters**, largely unsaturated. These esters can be used in the original concentrated form but the best practice is to mix them with classic diesel oil together and then to use this mixture as fuel for diesel motors. Conveniences: Biodiesel and classic diesel oil mixture can be used in present compression ignition engines with no special constructional adjustments of motors and in the frame of present existing infrastructure. [Department of Physical Chemistry](#)

New Discoveries

1. Prof. Gary Strobel from American State University in Montana has found a species of fungus able to produce hydrocarbon fumes (for example n-octane) as a waste product of its catabolism. On the top of it scientists have identified even certain amount of light alcohols and esters by virtue of mixture burns even more effectively than classic fossil oil. The name of this organism is *Gliocladium Roseum* and it lives commonly in Patagonia among the cells of the tree *Eucryphia Cordifolia* in mutual profitable relation. Kind of this symbiosis is well-known as mutualism. According to Prof. Strobel this fungus is only one organism in the world capable to make up it. He published his work in professional journal *Microbiology*. [Gary Strobel](#) The *Eucryphia Cordifolia* provides source of energy and nutrients for this micro-organism and on the contrary *Gliocladium Roseum* by hydrocarbons production protects this species of tree against the other parasites. Very interesting and important finding is that this organism is able to produce hydrocarbons some time under the laboratory conditions and mainly – it's able to utilize cellulose for production of hydrocarbons. And cellulose is one of the biggest and omnipresent, inexhaustible and renewable natural sources in contradistinction for example to vegetable oil or animal fat. But the Prof. Strobel's discovery has significance in term of molecular biology as well. After the recognition of responsible gene or group of genes it shouldn't be problem by using of modern techniques of molecular biology to transfer this genetic information into the different organisms and exactly and correctly to make incorporation of this information into the correct locus of the foreign genome. In this way this ability for hydrocarbons production could be transformed and extended as more universal biological quality of some of carefully selected organisms and finally all process industrialized. This biotechnology approach could become solution of oil crisis in the near future.
2. Members of research team (Phd.students) George Huber, Juben n. Chheda, Chris Barret and their leader Prof. James Dumesic from Technical Faculty at Wisconsin University in Madison (Ohio) worked out procedure how to obtain liquid alkanes from biomas-derived carbohydrates. They called their process as Aqueous Phase Reforming (APR). Recently, their APR process has been modified to produce alkanes from biomass-derived sugars. Alkanes ranging from C1 to C6 can be produced by aqueous phase dehydration/hydrogenation (APD/H) of sorbitol (hydrogenated glucose) by a bi-functional pathway. Sorbitol is repeatedly dehydrated by a solid acid ($\text{SiO}_2 - \text{Al}_2\text{O}_3$) or a mineral acid (HCl) catalyst and then hydrogenated on a metal catalyst (Pt or Pd). The biorefining of sugars to alkanes plus CO_2 and water is an exothermic process in which the products retain approximately 95% of the heating value and only 30% of the mass of the reactant. Larger liquid alkanes ranging from C7-C15, which could be used as a premium, sulphur free diesel fuel, can be produced by APD/H of larger carbohydrate-derived molecules. I suppose that this potential technology of the future can be finally successful in practical applications but investment and operating costs in projection for factory conditions can be indispensable. [James Dumesic](#)

B.1.3. Biodiesel Versus the New Technology Approach (A New Strategy)

Because vegetable oil eventually animal fat is a **common inlet commodity** in both of these cases, new technology approach (a new strategy) can be compared in a meaningful way just with present Biodiesel production. From whence it follows that this new strategy has got certain same disadvantages and advantages as well. The most important common disadvantage is fact that production of Biodiesel fully depends on harvest volume of basic raw material. Availability of this basic raw material is into the bargain finite because for example there's no chance to grow Rape (Swedish turnip) on the same piece of land every year (rape blossom beetle) and because only oil is used from whole plant for biofuel production. On principle volume of rape production never can be so sufficient in order to Biodiesel could fully compensate for classic diesel oil. This is the biggest limitation for the new strategy as well. Nevertheless the new technology approach can be better in other criteria. Number of these criteria is considerable and it will be subject of scientific and technology research. There is just list of qualitative comparative criteria between Biodiesel and New technology approach below:

1

- **biodiesel** - uses mostly methanol as a second reactant. Methanol technologically proceeds from the synthetic gas (CO and H₂ mixture) and relates to fossil sources of energy. In addition it is dangerous for human health and environment.
- **new strategy** – doesn't use any second reactant. Reactant is just one, fatty acid molecule.(FAM).

2

- biodiesel** – Fatty acids methyl esters FAME (100% biodiesel) with no classic diesel oil addition are very aggressive and corrosive towards rubber components of Diesel motors. FAME don't reach for power parameters of classic diesel oil. They have high smoke emission during combustion process, a bad filterability at low temperature (thaw point -8 degrees of Celsius) and very low caloric value. Second reason for necessity to mix FAME with classic diesel oil together is also high factory price of the final product. Mixture of FAME with classic diesel oil is greasier than diesel oil and so it cuts finally attrition of motor. [Department of Physical Chemistry](#)
- **new strategy** – main and final product is the close fraction resp. mixture of hydrocarbons with all positive combustion features and quality typical for any fuel on the base of hydrocarbons. No necessity to mix this final product with classic diesel oil together, high caloric value guaranteed. Final factory price of product can be same like in the case of Biodiesel production, maybe even lower.

3

- **biodiesel** – FAME are agglomerated at the contact with water therefore Biodiesel cannot be stocked too long time. But it's possible to use present existing infrastructure on the way between producer and the final customer.
- **new strategy** – Final product (hydrocarbons) hasn't got any disadvantages in term of this criterion. Also between producer and the final customer it's possible to use present existing infrastructure.

4

- **biodiesel** – operates the production process continuously.
- **new strategy**- operates the production process continuously.

5

- **biodiesel** – very good emission parameters during combustion process if aromatic hydrocarbons and sulphur compounds are properly obviated from petroleum part of biodiesel.
- **new strategy** – excellent emission parameters are expected.

6

- **biodiesel** – If aromatic hydrocarbons and sulphur compounds are properly obviated from petroleum part of biodiesel then this biofuel has got an excellent biological decomposability. 95% of biodiesel is decomposed during 28 days.
- **new strategy** – Very good biological decomposability is also anticipated. Reason is that product is chemically linear aliphatic hydrocarbon containing in average relatively big amount of double bonds in the chain of carbon atoms. These linear systems are accessible for degradation enzymes of some of micro-organism species as well.

7

- **biodiesel** – it is basically a closed-cycle technology. Certain problem is manufacturing waste water that can content some amount of residual methanol and soups, possible contaminant matters for environment. But Biodiesel technology is not all over closed production cycle. In use catalysts, NaOH, KOH ev. H₂SO₄) are slowly and progressively used up and they have to be still added into the system. The next three production methods (heterogeneous catalysis – using of organo-metalic complex compounds or solid catalysts as zeolitic structures or some metal oxides – MgO, enzymatic catalysis – Rizhomucor miehei, Pseudomonas cepacia, Caida Antarctica eventually production process with no using of any catalyst) are still in phase of research and development. [Department of Physical Chemistry](#)
- **new strategy** – It's also basicly closed-cycle technology. No problem with manufacturing water, no contamination of living environment.

8

- **biodiesel** – it's basically non-waste technology. All secondary products are useful and fully exploitable. (glycerol, fatty acids, oil seed cake).
- **new strategy** – it's basically non-waste technology as well. The same secondary products like in the case of Biodiesel and one new secondary product in addition.

9

- **biodiesel** – combustion criteria are well-known
- **new strategy** – combustion criteria of the product are not well-known. But it's possible to remark that with regard to anticipated very close and stabilized fraction of linear and mostly unsaturated aliphatic systems (C₁₅ –C₁₉), very interesting findings within the context of common criteria of octane versus cetane index can be expected.

10

- **biodiesel** – It's a hazardous workplace in term of working and safety conditions.
- **new strategy**- In light of labour protection it will be possible to ensure perfect working conditions for operating staff.

11

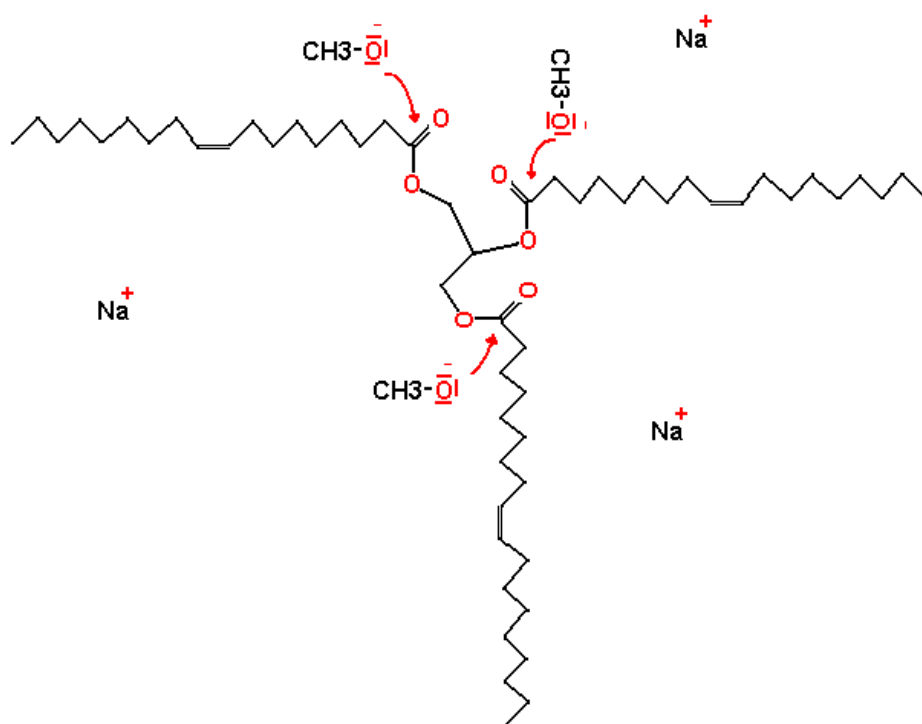
- **biodiesel**- Production process is problematic. Production is very often put out of operation in consequence of fluctuations of physiochemical and hardly controllable fixative balances.
- **new strategy** – Continual process of production could be trouble free in term of chemical and operating conditions. Just one reactant, no fixative balances, no water.

B.1.4. Critique of the Present Technology of Biodiesel Production

From chemical point of view production of biodiesel (FAME) is trans-esterification. On the bases of previous comparison it's possible to state positive prognosis of this technology for the near future.

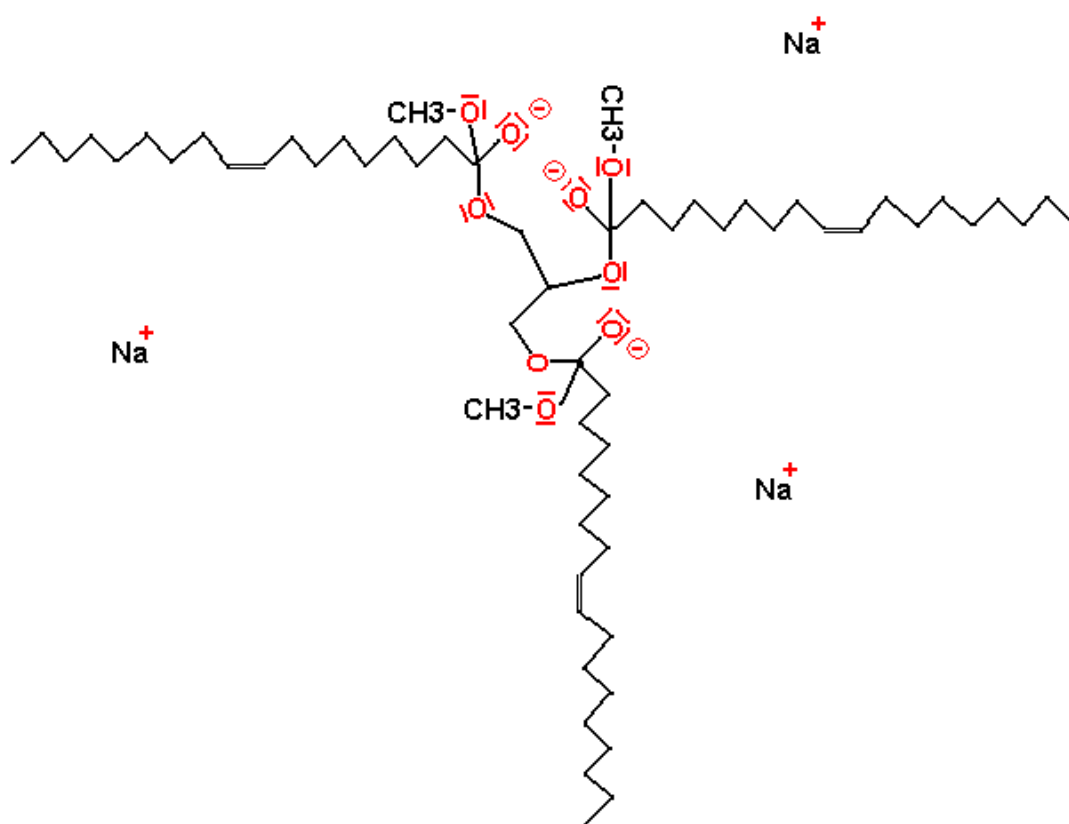
However this technology has many troubles from another point of view - namely from view of the mere technology and operational process. Final product of the factory ester interchange units is then methyl ester of fatty acids (fatty acids methyl ester FAME) suitable just for compression ignition oil engines. Process of continual FAME production is also relatively energy-demanding and above all demanding of operating staff and the special computer programme control coming from the central control station. Approximately every two hours there is necessity to take samples from about 10 sampling points of the factory and bring them into central laboratory for analysis. Continuity of production is so practically just the only advantage. Process is multi-factorial and SOAPS are the biggest trouble and adversity of all this technology. Soaps can be generated by presence of water in input (entering) methanol and by partial hydrolysis of product within separation processes. During separation process there is water phase containing methanol, sodium hydroxide, alkaline phosphates, soaps and glycerol and some amount of fatty acids as well subsequently separated in a physiochemical way and in a post-reactor part of production procedure from organic phase which contains except the very methyl ester even free fatty acids, glycerol, water, alkaline phosphates and spent or again by hydrolysis generated methanol. All under just about 60 degrees of Celsius if all process is catalyzed with alkaline hydroxide and if methanol is used as a second reactant. (30 degrees of Celsius for ethanol).[Department of Physical Chemistry](#) Basically and in a physiochemical way it is multiphase system mutually conjugated and with difficulty controllable solutions. Really basic problem of this technology is to hold – **on principle** – variations and fluctuations in the frame of physico-chemical fixative processes –balances- between water and organic phase. Even if whole continual process is managed and controlled by special software facility, process production has to be sometimes shut down completely and started up again. Economic and operating costs of separation process are relatively significant. Alkaline hydroxide has to be added into entering and toxic methanol first and before enter into the pre-reactor part of technology process. In consequence of it and in the frame of chemical dynamic equilibrium which is distinctively displaced (shifted) to the left side - then to the side of starting compounds (reactants) – it will come about generation of very reactive and nucleophilic metoxyl anion (MeONa) and neutralization water. It means that water cannot be - as a matter of fact - removed from methanol even before entering of methanol into the process. Metoxyl anion as a very strong nucleophilic particle attacks the ester group in triacylglyceride molecule in accordance with following and very simple reaction mechanism: (Figure 1)

Figure 1.



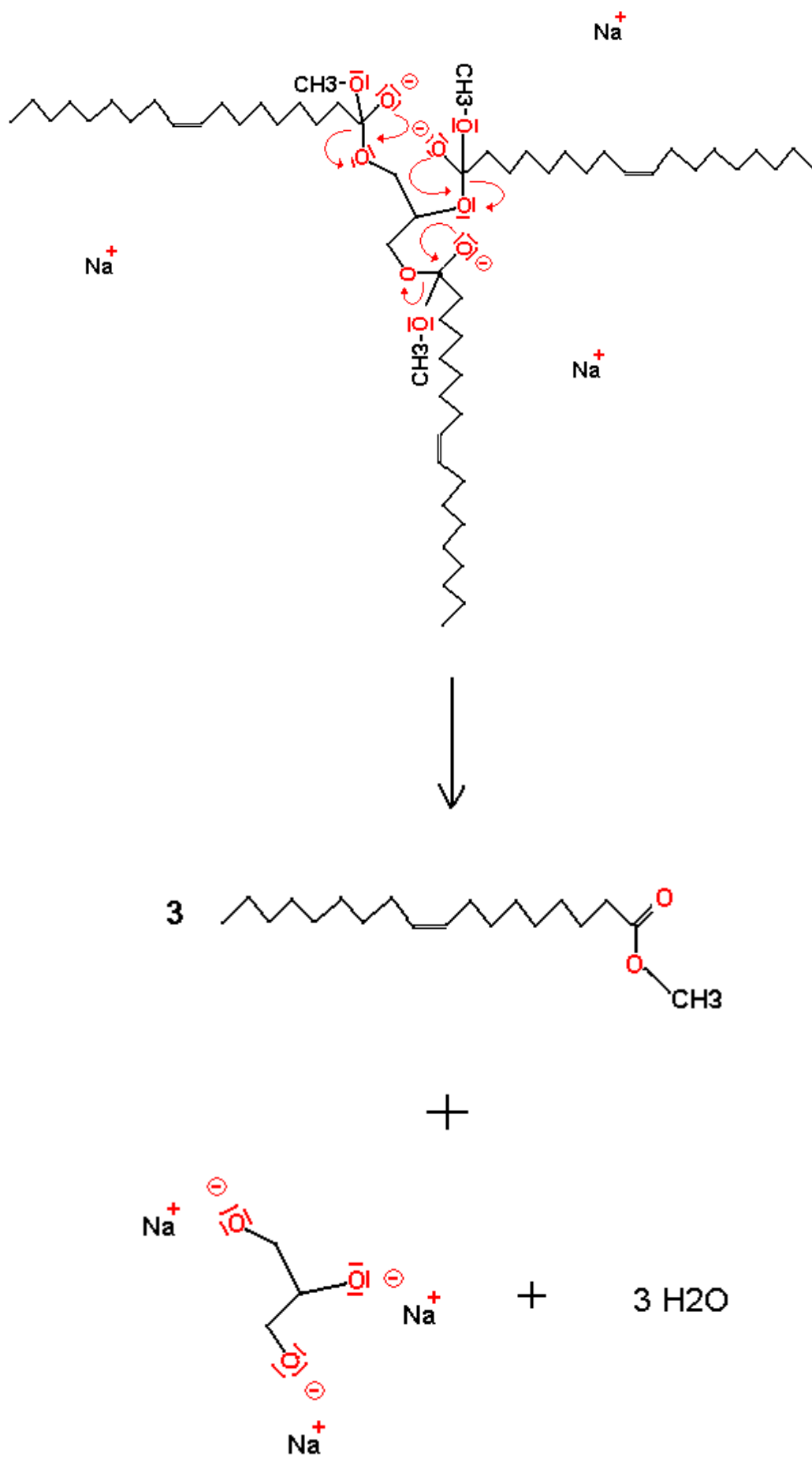
As the simplest example of neutral triacylglyceride - concretely ester of glycerol with cis-9-octadecene acid - familiarly oleic acid - can be chosen. All natural Fatty Acids Molecules (FAM) have on all their double bonds between carbon atoms only cis-configuration, all of them are just mono-carboxylic, linear and all have got just even number of carbon atoms in the chain. (This fact reflects biochemical mechanism of FAM synthesis which is basically inverted Linen's spiral where construction of carbon skeleton goes on by means of two-carbon atoms acetyl coenzyme units under energetic doping coming from adenosine triphosphate (ATP) and specific enzymatic catalysis inside of the living cells.) There is situation of simultaneous three methoxyl anions approaching reaction centre which is electrophilic carbon atom of the ester group in the figure 1. But this is just special case of simultaneous attack. In reality more likely successive attack within very short time interval is expected. In this manner there's a transition stage generated on reaction centres with tetrahedron geometry on them and also with transferred electric charge. See figure 2.

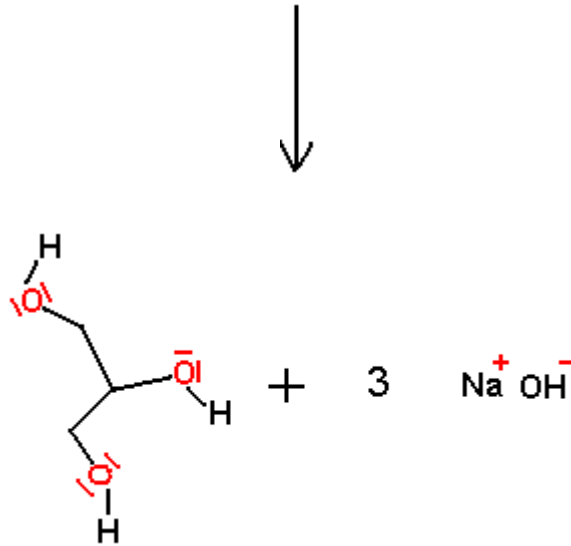
Figure 2.



This model transition stage will release molecule of FAME by electron pairs pushing and at the same time anion of glycerol with very brief life period. This anion is hydrolyzed very fast in reaction medium giving glycerol molecule (1,2,3 propane-triol) and 3 sodium hydroxide equivalents. See figure 3.

Figure 3.





The mere process of biodiesel production is then relatively demanding in energy and procedural way. That's why maybe final product of trans-esterification production units – FAME – is so much expensive. The next and last point of view is ecological. Although this technology can be considered as highly environmental in term of carbon dioxide production during combustion process of biodiesel and utilization of this gas at photosynthetic assimilation, on the other hand manipulation with methanol requires appreciable circumspection in all safety parameters because methanol as a dangerous substance for human life and environment is processed and used in heavy amount. Manufacturing water is though recycled with by system however leakages into sewerage water and contamination of environment are not absolutely foreclosed.

B.1.5. An Indirect (Conditioned) Fatty Acids Decarboxylation As Alternative Technology Approach

B.1.5.0. A Main Criterion of the Project

A main criterion of all project is the postulate to operate future technology process continuously. All steps of this project will be subordinated to this important criterion.

B.1.5.1 Central Idea of the Project

From strategic and chemical point of view the project is based on profoundly and qualitatively different principle. Central idea is transformation of fatty acid molecule to hydrocarbon with one carbon atom less. Subject of the project is problems of realization of industrialized viable, for investment not too much expensive, continuously operated and at the same time through the front-end regio-selective dehydrogenation facilitated decarboxylation. Project is highly comprehensive and expressively economically and ecologically oriented. See details in B.1.3. Part.

Environmental point of view: Supposedly the most important fact could be absolutely well-balanced "score" between carbon dioxide emission and its utilization during the course of photosynthesis if main final product (C15 –C19 hydrocarbons) will not be mixed with classic diesel oil together. This biogenic hydrocarbon fraction **can be** but also **doesn't need to be** mixed with fossil diesel together whereas

FAME (100% Biodiesel) **has to be** mixed with fossil diesel together. Failing which Diesel motor requires constructional adjustments.

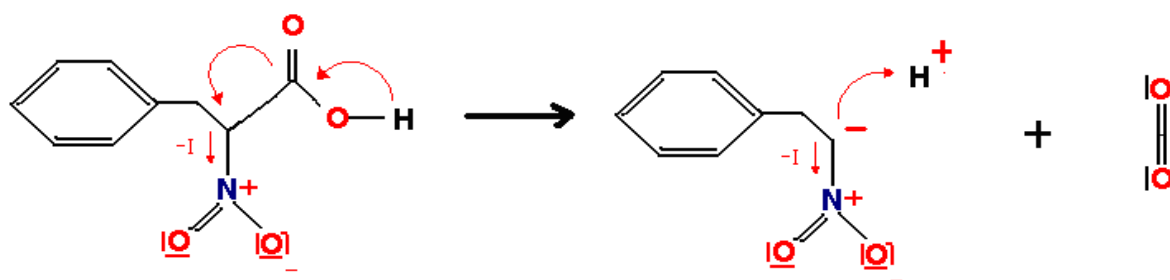
Economic point of view: Because the new technology approach is to be compared with the present production of Biodiesel (see 11 criteria above), **it is possible** to assert that operating costs (not investment costs) **can be even lower** than in the case of Biodiesel production if new potential technology process will operate under the mild reaction conditions. Connection between the front-end regio-selective dehydrogenation with the consequent and spontaneous decarboxylation can make the best expectations for it.

B.1.5.2. Summary of Organic Acids Decarboxylation Reactions

B.1.5.2.1 Unsuitable Candidates in Light of Main Criterion

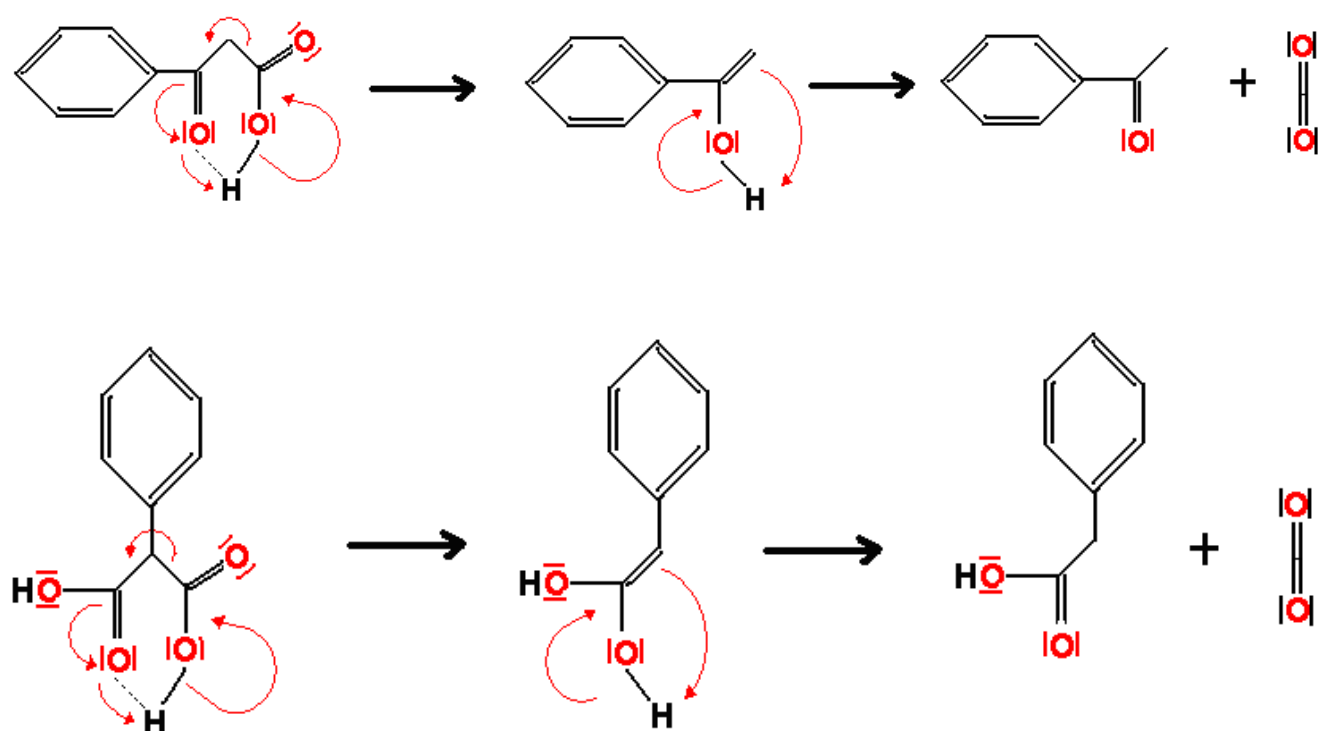
If we will consider the mere decarboxylation reaction in term of pure chemistry, not in term of industrial applications, then it is in operation that there're considerable differences among particular structural types of organic acids. Carbon dioxide elimination can be realized depending on molecular structure by heating at temperatures about from 100 – to 300 degrees of Celsius. Carbon dioxide molecule can be the most easily removed from acids containing electronegative substituents in the alpha position towards carboxylic group of atoms (NO₂, CN, halogen etc.). [Organic Syntheses Page 236](#) As an example it's possible to choose 3-phenyl 2 nitro-propionic acid like in the figure 4. Driving force of this type of decarboxylation is formation of stabilized carbanion in consequence of negative inductive effect of nitrogroup against the alpha carbon atom where formal sum of solid negative charge and relative decrease of electron density on alpha carbon atom is lower than 1. It's example of so called field effect stabilization of carbanion. See figure 4.

Figure 4.



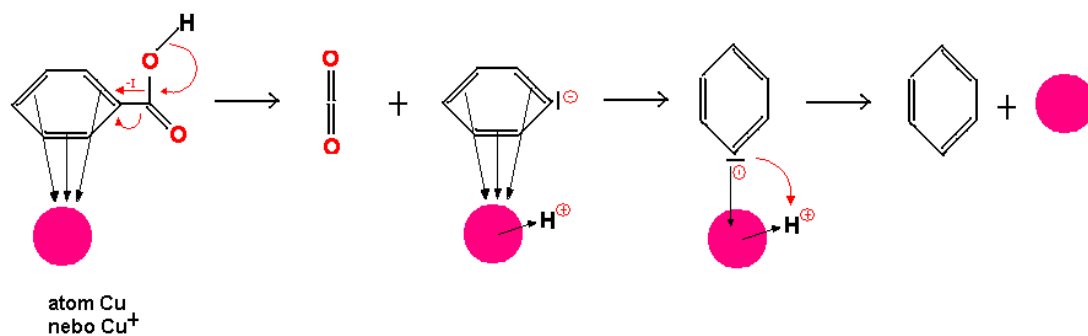
Beta oxo acids and substituted malonic acids also release very easily carbon dioxide molecule. [Organic Syntheses Page 236](#) There's different kind of driving force there in reaction mechanism. The reason is easy formation of cycle transitory state which is very well stabilized. See figure 5.

Figure 5.



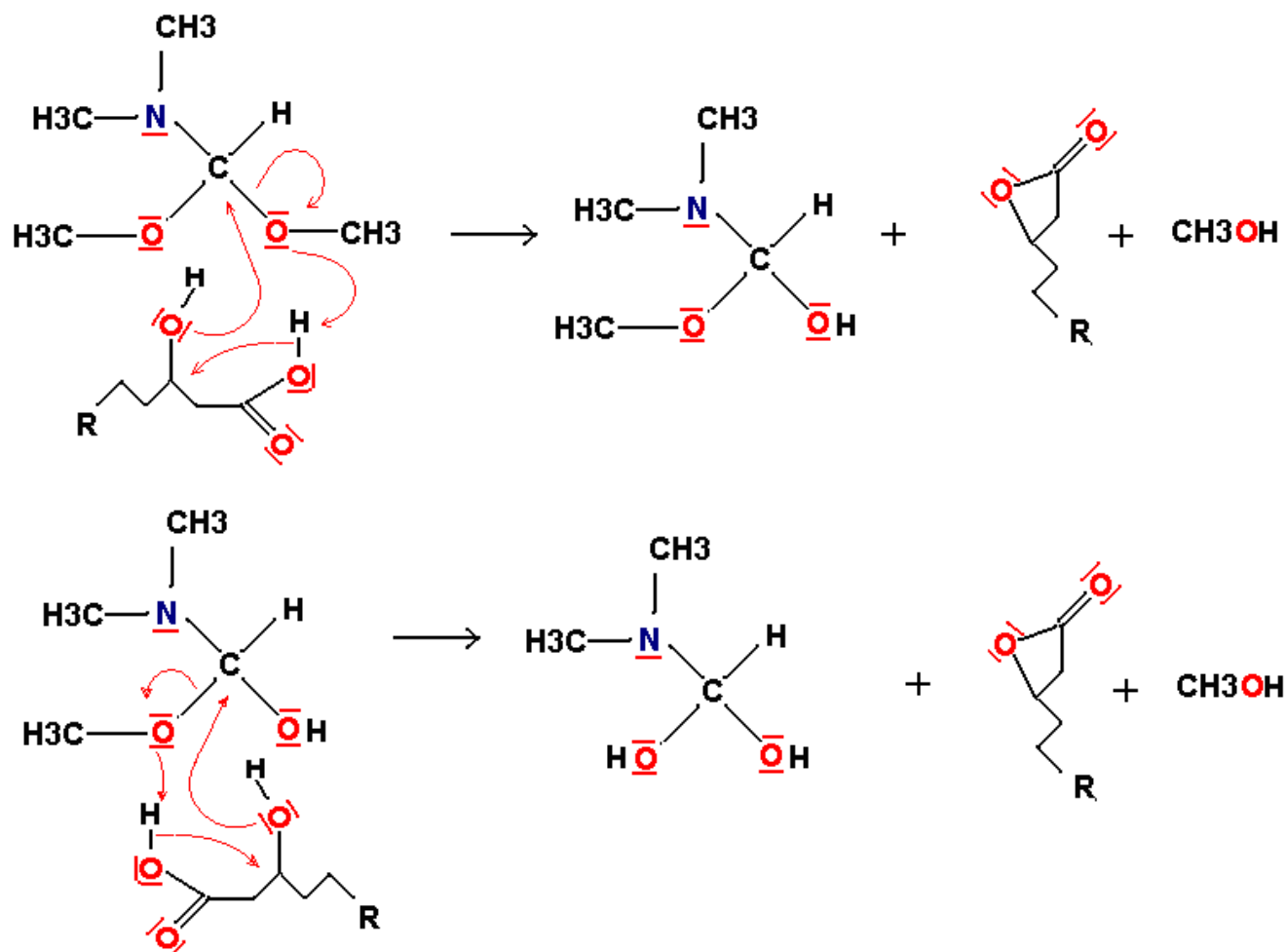
Aromatic and heteroaromatic acids without any activating atomic groups eliminate carbon dioxide by heating in high boiling amine in the presence of copper cations with oxidation state +I or by direct heating up with copper powder. [Organic Syntheses Pages 236-237](#) Reaction mechanism is hypothetical and proposed by me. Possibly and first we can anticipate formation of polynuclear complex of aromatic nucleus on a donor – acceptor π - complex bases with copper atom or copper +I cation in the centre of symmetry of the complex. Because system of 6π electrons is formed by LCAO process (Linear Combination of Atomic Orbitals) where 6 degenerate and singly electron occupied 2p atomic carbon orbitals are combined, as a result there are 6 molecular orbitals obtained, varying in energy in the frame of all system. 3 of them are binding and other three are anti-binding. All of three binding molecular orbitals contain three electron pairs each with opposite spin but just one of them has got the lowest energy. Next two electron pairs occupy two binding orbital with higher energy than previous one and both of these orbitals are degenerated. And just these two electron pairs coming from HOMO (Highest Occupied Molecular Orbitals) can participate more easily on formation of donor - acceptor π - complex and to enter transitorily into two unoccupied d – orbitals of copper atom after the next additional overlap of vacant d-atomic orbital of copper atom with one of the fully occupied HOMO. The final effect of this complex formation can be decrease in electron density of aromatic nucleus and in consequence of it negative inductive effect could be generated. This temporary negative inductive effect could increase of reactivity of the complex and by shift of electron pairs could facilitate decarboxylation as a result. Intermediary and unsteady phenylide carbanion could at the same time neutralize with proton accession. See figure 6.

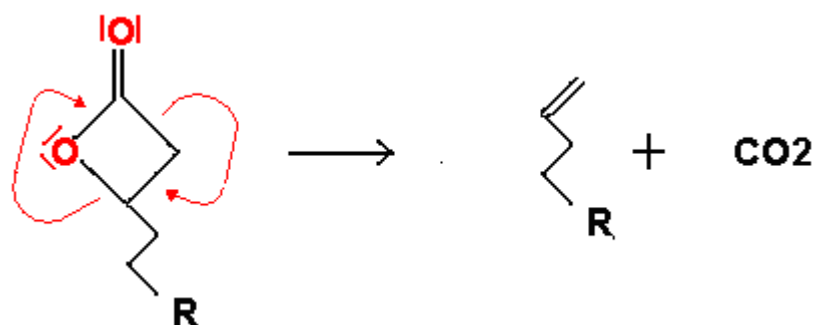
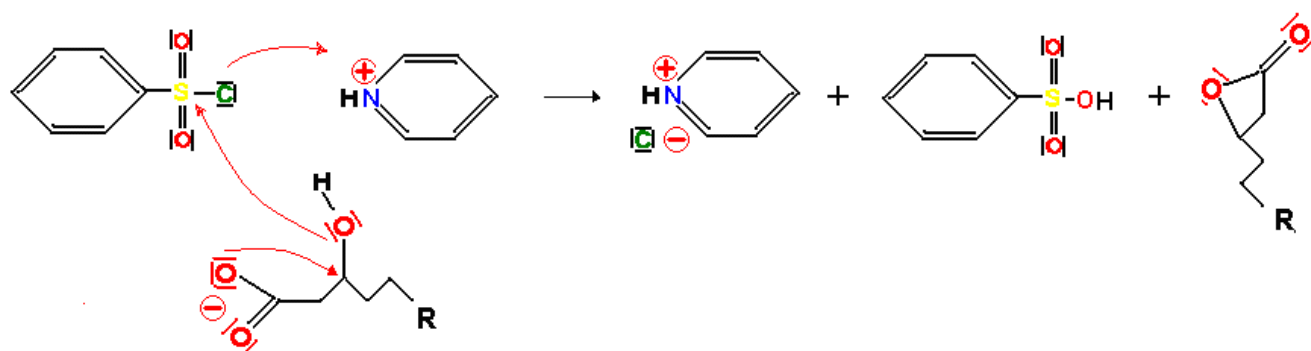
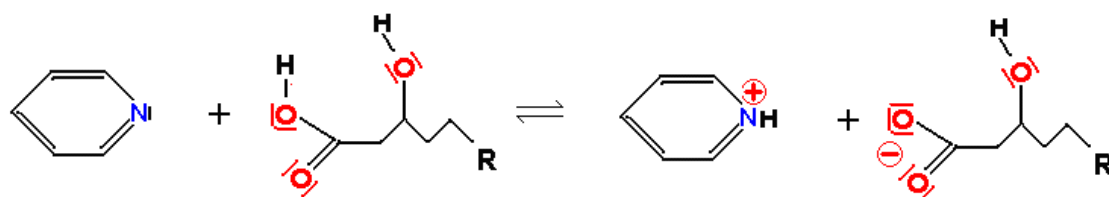
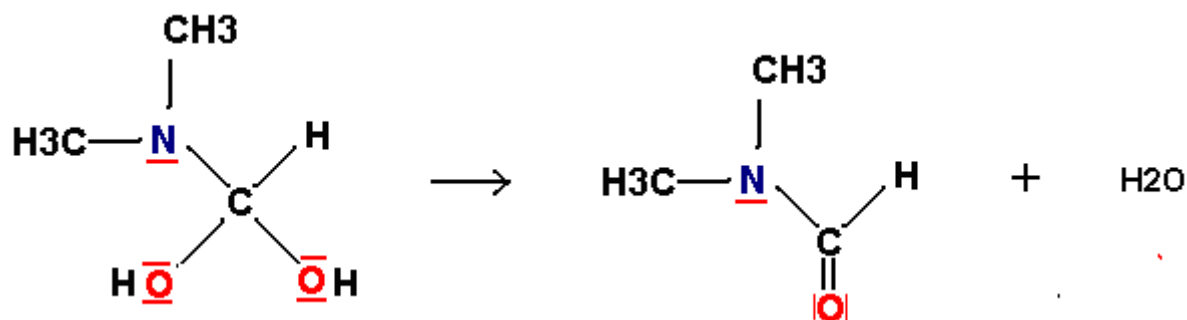
Figure 6.



Transformation of beta-hydroxyacids into substituted alkenes – olefins is also synthetically interesting. It's running very easily at heating in overflow of dimethylacetal of N,N –dimethylformamide or in mixture of benzene sulphonyl-chloride with pyridine. Reaction is stereospecific (syn-elimination) and temporary origination of beta-lactones as an intermediate product is supposed. The mere beta-lactones also release carbon dioxide molecule by pyrolysis. [Organic Syntheses Page 237-238](#) Driving force of lactonization could be by monomolecular mechanism realized connection between carboxylate anion with activated beta-hydroxylic group or rather with regard to stereospecific character of reaction by more probably bimolecular mechanism realized cyclic transition stage which is distributed into products by synchronic shift of electron pairs. Mechanism is also hypothetical and proposed by me. See figure 7.

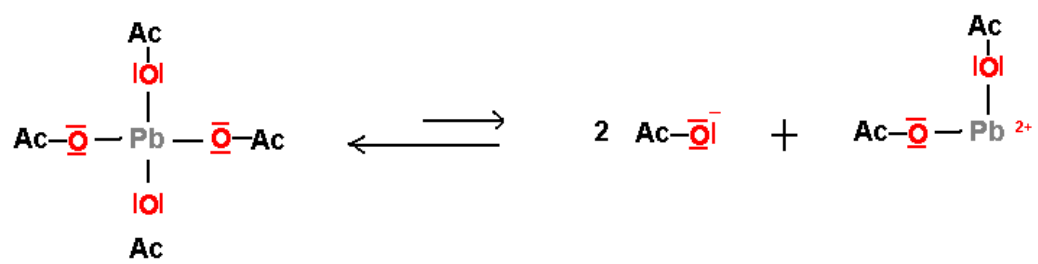
Figure 7.

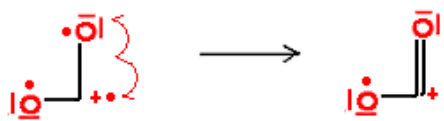
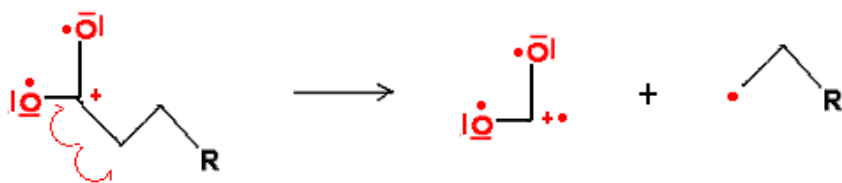
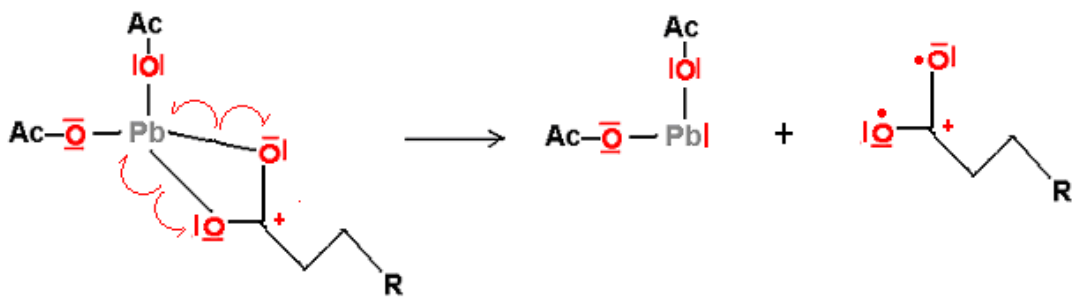
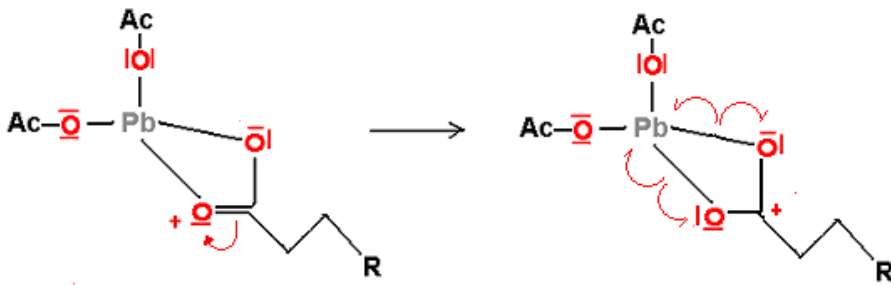
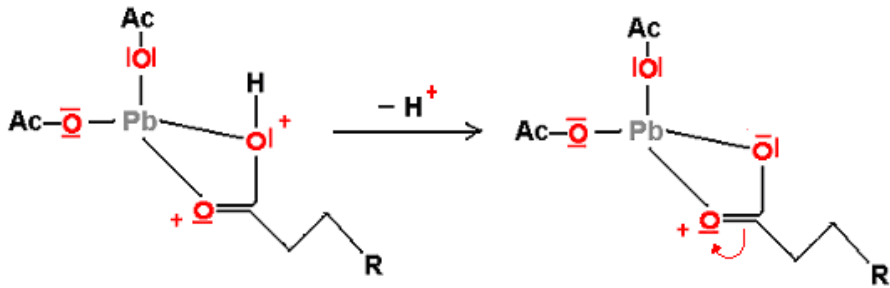
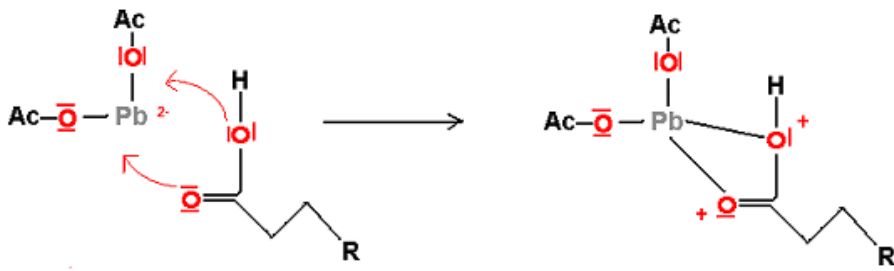


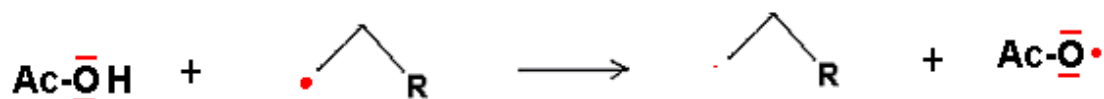
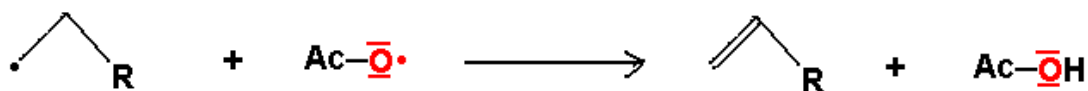
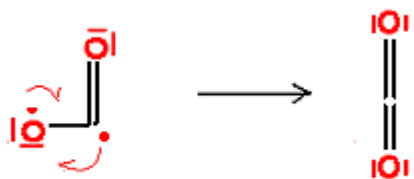
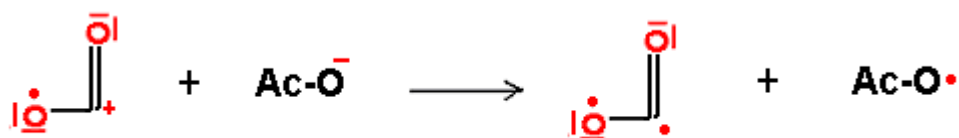


In term of reaction mechanism the oxidative decarboxylation of free acid by virtue of lead tetraacetate is also interesting. Reaction proceeds in aprotic non-polar solvents (benzene, xylene, toluene etc.) However alkanes and alkylacetates are formed as well. Alkylene formation is supported by +II cupric salts that oxidize (single electron transfer – SET) rising alkyl radicals into carbocations (carbenium cations). [Organic Syntheses Page 237](#) Proposed mechanism is also hypothetical and doesn't need to relate to reality. It could be conformable to well-known mechanism of oxidative fissure of vicinal diol molecule into two molecules of aldehyde by the medium of lead tetraacetate or alkaline periodate eventually even other reagents with bulky central atom that has a large polarizability. The meaningful mechanism could look like in the figure 8.

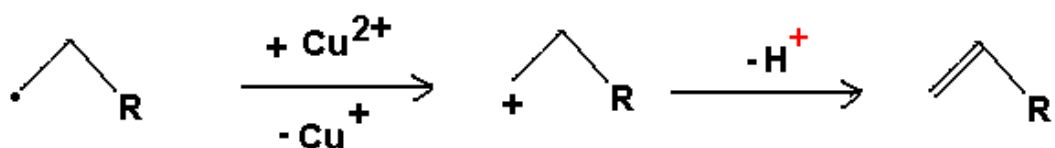
Figure 8.







After +II cupric salt addition (CuSO_4) there's preferred terminal olefin formation in the mechanism. +II cupric cation so actually officiates as electron transmitter and catalyst as well. It's example of single electron transfer again. Initiation for alpha-olefin formation is oxidation of primary or after hydrogen atom fault better stabilized secondary alkyl-radical into carbenium ion and formation of double bond by proton elimination from nearby carbon atom. In presence of +II cupric ion reaction mechanism is then enriched and focused selectively on alkenes.



+I cuprous kation can be re-oxidized for example by reaction:

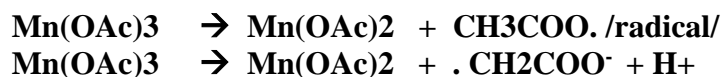


This decarboxylation activity is not restricted just to plumbum in oxidation state +IV, it also concerns next ions of the transitory metals. Their decarboxylation activity is opened out in series showed in following table.

Relative speed of oxidative decarboxylation:

Relative Speed	Ce⁴⁺	Ag²⁺	Pb⁴⁺	Co³⁺	Mn³⁺
	1	2	20	100	500

For example Mn³⁺ reacts with acetic acid in several ways:

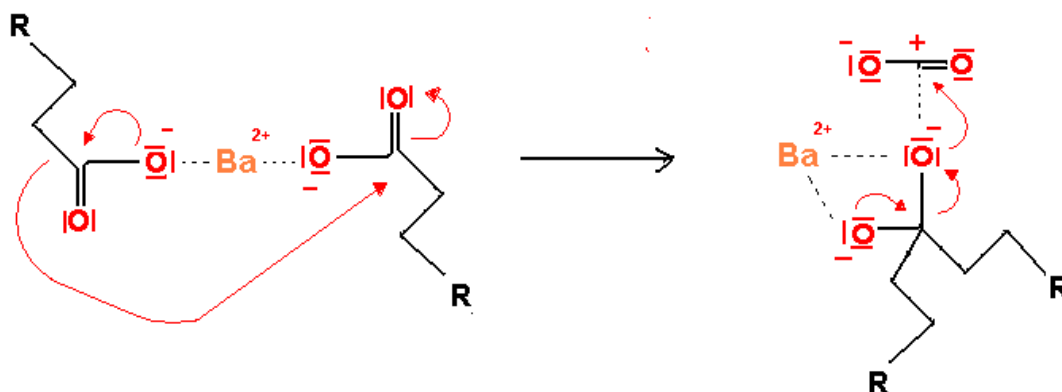


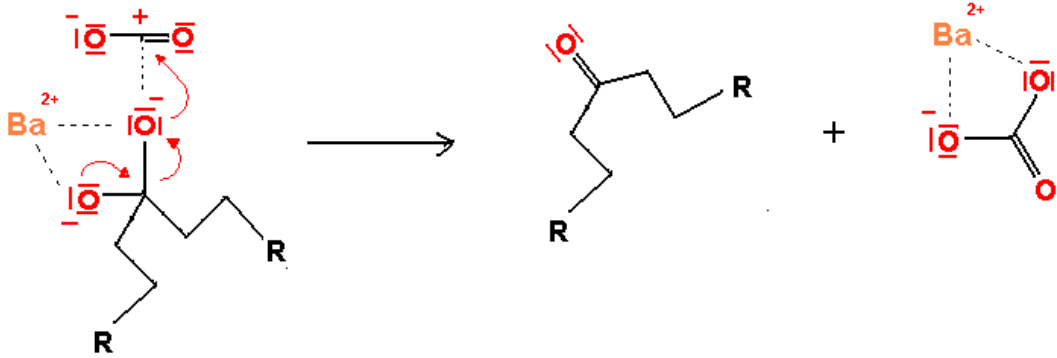
Both reactions run over 150 degrees of Celsius very fast. Formed radicals then crumble for example into carbon dioxide and methyl radical. [google – relativni rychlost oxidativni dekarboxylace](#)



If we discuss alkane acids without any activating groups in the face of carboxylic group which is just case of fatty acids, so in term of simple chemical transformation of decarboxylation character it's possible to refer to basically and only ketonic decarboxylation pyrolysis of calcium or baric salts, latterly and better using of ThO₂ (thorium oxide) in gaseous phase [Organic Syntheses Page 237](#) or dry distillation – pyrolysis of alkaline salt of alkane acid under the one-molar overflow of alkaline hydroxide. Possible mechanism of ketonic decarboxylation pyrolysis is showed in the following figure 9:

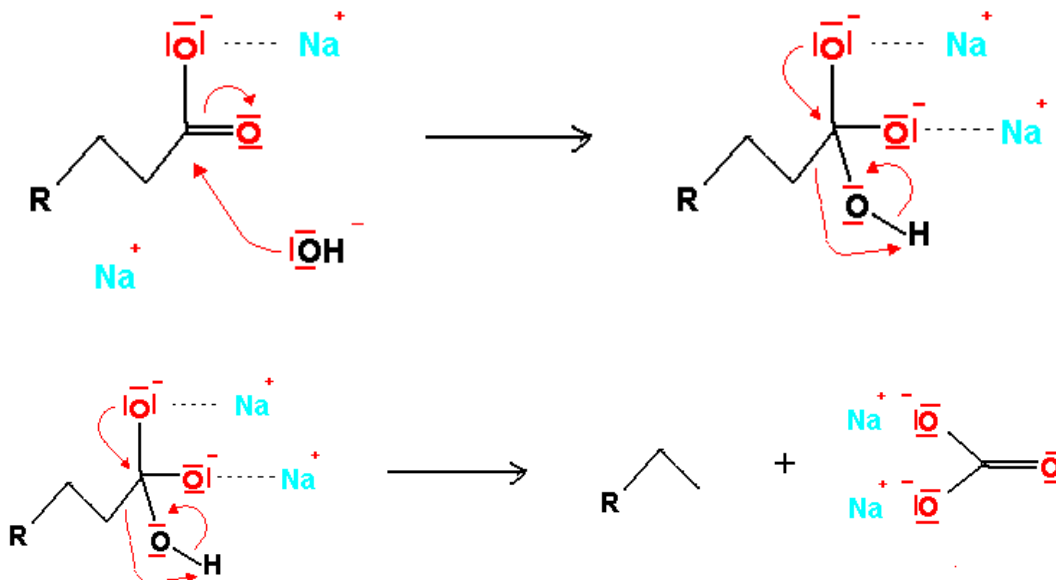
Figure 9.





Mechanism of the dry distillation – pyrolysis of alkaline salt of carboxylic acid under the one-molar overflow of alkaline hydroxide is following: (Figure 10)

Figure 10.



At this point of syllabus it's wholesome to recall that target of the project is then building of functional and fully computerized pilot plant where as the main criterion is **continual operation**. However if we call in question this and almost comprehensive enumeration of decarboxylation reactions, we have to submit in most of cases that inclination to potential future technology in accordance with main criterion of the project doesn't coincide with fundamental of most of forenamed reactions But namely and especially in the case of **fatty acids molecules** we can speculate basically just about examples presented in the figures 8 and 10. The mere fatty acids ever don't give way to decarboxylation in their free and then non-dissociation form. However even in these cases (figures 8 and 10) main criterion of the project wouldn't be possible to perform. One of the indispensable reasons is using of more than just one reactant. And necessity to use more than just one reactant implicates almost necessity to operate technology discontinuously, at least within the frame of the main production unit, respectively within the scope of a main reactor and all its additional and accessory equipments in chemical industry sector. Of course, discontinuous process doesn't mean that final and main factory product cannot be removed continuously. But this claim logically and necessarily leads to building up and processing of series of identical and parallel reactors which are involved in timed cycles in such a way in order to the final product could be removed (exhausted) from the whole factory process continuously. As a very factual example it's apropos to mention PVC production, concretely in Spolana Neratovice Company (The Czech Republic). There are 14 identical reactors there. Whereas discharging is finishing in one of them, the valve for discharging is starting to open out in the next one, in several ones the mere polymerization

situation could look like in the figure 13: Illustrated intervals of boiling points relate to using of atmospheric pressure. Figure 13.

Figure 13. (ex)

One of preconceived but totally hypothetical and meantime very idealized model of the central part of the factory process for continual hydrocarbon fraction production on the bases of fatty acids could look similarly like in the figure 14:

Figure 14.

1st .Virtual Period

This period will be important mainly for PC programmers and organic technologists. Target of this period is origination of genetic computer programme that will be able to simulate dynamically all continuous technology process. PC simulation of the process will focus on monitoring of **operational, economic, safety and environmental aspects**. Operational aspects monitoring will cover influence of changes of individual variable quantities on whole system behaviour. Economic aspects monitoring will become task for industrial economist and cover balance analysis of investment and operational costs in projection to big-plant conditions. This dynamic model should enable industrial ecologist to consider carefully all accessible safety and environmental hazards.

2nd .Design Period

This period will cover activity bound for origination of the **project documentation for building of the pilot plant**. Organic technologist will focus on technology model origination (materials, valves, feedback networks, pick-up elements, pumps, heatings, heat exchangers etc.). After project documentation origination project can be moved up into the next part.

B.2.3. Realization Part

This constructional part of the project will include actual **building of fully automated and continuously working pilot plant**. After the final building approval the project will move up into the test pilot part.

B.2.4. Test Pilot Part

Test pilot part of the project will cover monitoring of all operational, economic, safety and environmental aspects during the course at least of one calendar year.

B.2.5. Conclusion of the Project

All positive and negative findings of the test pilot part of the project will become content of this final conclusion. On the bases of this final critical assessment it will be possible to perform comparison between Biodiesel production and this technology in all accessible parameters and make objective prognosis of this technology approach for the future.

B.3. Human Resources – List of the Specialists

Project will be assured by author of the project in conjunction with the following creative staff:

Mathematician:

01.....

02.....

PC programmer and specialist for PC simulation analysis and modelling:

03.....

04.....

Organic technologist:

05.....

06.....

Industrial economist:

07.....

Ecologist: 08.....

C. Eligibility of Applicant and Submitter

C.1. Research Technical and Material Conditions of Applicant for Research

Applicant has got sufficient material and technical facility that allows him to solve project without necessity to buy new equipments. Computer equipment is fitted with software (MS 2000XP,mS Office XP etc).

C.2. CV of Research Workers

Mr. Mgr. Martin Skoda - Author of the Project

Date of Birth: 8th April 1964

Place of Birth: Liberec, the Czech Republic

Nationality: The Czech Republic

Education:

1979 – 1983 Agricultural and Technical Secondary School in Frydlant v Cechach with leaving examination

1987 -1991 Pedagogy University in Hradec Kralove.Certificated for 2nd stage teaching in teaching qualification for biology chemistry and pedagogy.

1998 - Simultaneous entrance to Phd. study programs at two Universities. University of Chemistry and Technology – Department of Organic Chemistry, Prague. Biological Faculty of South Bohemian University in Ceske Budejovice, specialization: Cell and Molecular Biology. Both study programmes were immatured.

Employment and Practical Experience:

1983 -1986 Agronomist

1991 – 1993 Assistant professor – East Bohemian Museum in Hradec Kralove, Department of Natural Sciences

1993 – 1994 Teacher at the Primary school

1994 - 1996 Laboratory technician – Biodiesel Mydlovary, Zliv near Ceske Budejovice

1996 – 2000 Teacher at the Secondary school – English, Biology, Chemistry

2000 – 2002 Research worker - Research Institute for Inorganic Chemistry in Usti nad Labem

2002 – 2004 Production Operator – Spolana Neratovice – PVC production

2004 until now – Chef and Machine Operator in United Kingdom (see additional CV)

Competence and Certificates – College Diploma

Member of the Czech Chemical Society since 2001

Practice and experience in organic technologies, namely Biodiesel production, PVC and polystyrene production.

Mr.Ing. Joseph Navratil – Applicant of the Project

Date of Birth: 27th May 1945

Education

1960 – 1963 Secondary school SVVS Decin – leaving examination

1966 – 1972 Faculty of Building of Technical University in Brno

Employment and Practical Experience:

1964 – 1964 Operator – Machine-Works - Decin

1972 – 1974 Master Builder – Highway Cooperation n.c. Brno-Prizrenice

1974 – 1980 Officer – Mest.NV – Department of Construction Boskovice

1980 – 1985 Preparator of Investments – Letostroj n.c. Letovice

1985 – 1987 Supervisory Engineer – Ingstav Brno
1987 – 1988 Supervisory Engineer – Prumstav Pardubice, Concern Usti

1988 – 1989 Teacher – KNV – Department of Education

1989 – 1991 Teacher – SmKNV Ostrava – Department of Education

1991 – 2007 Builder - Construction Company JONA

2001 – 2001 Teacher – OU (district authorities) Department of Education Decin

2001 – 2001 Teacher – OU (district authorities) Department of Education Decin

2003 – 2004 Teacher – OU(district authorities) and PrS Decin XXXI

Competence and Certificates: - College Diploma
- Trade Certificate

After taking one's degree I was married since my 27 years old for 15 years. Since 1986 I'm divorced. I've got two sons. My number one hobby is theoretical physics since 1981. After democratic revolution I established a small building company in 1991 that was in progress till 1996. Then its business activity was reduced owing to debtors and prolonged legal disputes. Now I'm a pensioner and deal with theoretic physics as an amateur.

C.3. Summary of the Previous Activities

C.4. Specifications of Previously Processed Data

C.5. Next Certificates Evidential of Applicant's and Author's Qualification

D. Declaration that Author and Applicant will Respect All Conditions of Project Realization for Achieving of Targets and Parameters of the Research Project

E. Draft of Contract

F. Estimates and Confirmed Costs for Solution of the Project

References:

Department of Physical Chemistry, University of Chemical Technology Pardubice, the Czech Republic
Doc.Ing.Frantisek Skopal.CSc,Ing.Martin Hajek Ph.D.,Doc.Ing.Jaroslav Machek CSc, Doc.Ing. Karel Komers CSc, Ing.Jiri Kwiecien, Ing. Michal Cernoch. Biodiesel (FAME) Compensation for fossil oil, Science and Research

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<http://209.85.129.132/search?q=cache:OVAKqg7->

[wwwCMJ:www.jergym.hiedu.cz/~canovm/barva/r/o.html+relativn%C3%AD+rychlost+oxidativn%C3%AD+dekarboxylace&hl=cs&ct=clnk&cd=1&gl=cz](http://www.jergym.hiedu.cz/~canovm/barva/r/o.html+relativn%C3%AD+rychlost+oxidativn%C3%AD+dekarboxylace&hl=cs&ct=clnk&cd=1&gl=cz)

Organic Syntheses – Introduction and Selective Transformation of Functional Groups

Vaclav Dedek, Ladislav Leseticky, Frantisek Liska, Ivan Stibor, Jiri Svoboda

Department of Organic Chemistry, Charles University Prague 1994

Plus Table →

